**SUPPORTING INFORMATION**

# Olefin Hydroarylation Catalyzed by (Pyridyl-Indolate)Pt(II) Complexes: Catalytic Efficiencies and Mechanistic Aspects

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## EXPERIMENTAL SECTION

**General Considerations.** All reactions and experiments, unless otherwise noted, were performed using standard Schlenk techniques under $N_2$ atmosphere or inside a $N_2$ glovebox. Schlenk glassware was oven dried overnight before use and N-N$^-$ ligated metal complexes were stored at ambient temperature in a $N_2$ glovebox. Solvents were stored over 3 Å molecular sieves after drying with a JC Meyers Phoenix SDS solvent purification system. Solvents for organic syntheses were used without further purification. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratory. Benzene-$d_6$ was degassed by three freeze/pump/thaw cycles and then dried over 3 Å molecular sieves.

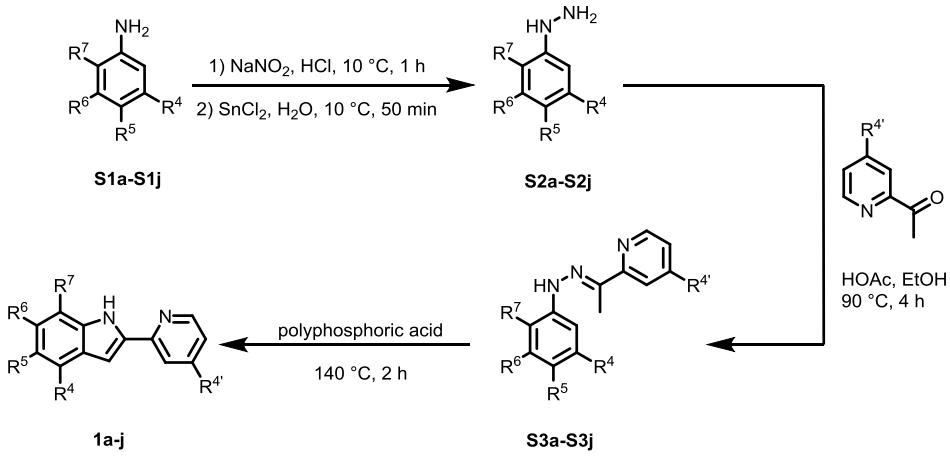
Ethylene (99.9%) was purchased in a gas cylinder from Praxair Technology and used as received. Propylene (99.99%) was purchased in a gas cylinder from Matheson Tri-Gas and used as received. *o*-Ethyltoluene, *m*-ethyltoluene, *p*-ethyltoluene, NaO$^t$Bu, AgOTf, PhLi, 2,6-di-*tert*-butyl-4-methylpyridine, and tridecane were purchased from commercial sources and used without further purification. $Si(SiMe_3)_4$ was purchased from a commercial source, sublimed before use, and stored in a $N_2$ glovebox. Phenyl hydrazine (**S2a**), 4-methoxyphenyl hydrazine hydrochloride (**S2e**), 4-methylphenyl hydrazine hydrochloride (**S2f**), 4-fluorophenyl hydrazine hydrochloride (**S2g**), 4-chlorophenyl hydrazine hydrochloride (**S2h**), 4-bromophenyl hydrazine hydrochloride (**S2i**), and 2-chlorophenyl hydrazine hydrochloride (**S2j**) were purchased from commercial sources and used without further purification. 2,5-Difluorophenyl hydrazine (**S2b**),[1] 2,3,4,5-tetrafluorophenyl hydrazine (**S2c**),[1] 4-*tert*-butyl-2-acetylpyridine,[2] *cis*-$(SMe_2)_2PtPh_2$,[3] $[(\mu\text{-}SEt_2)PtPh_2]_2$,[4] and $[(C_2H_4)Pt(\mu\text{-}Cl)Cl]_2$ (Zeise's Dimer)[5] were prepared according to published literature procedures.

All $^1H$, $^{13}C\{^1H\}$, and $^{19}F$ NMR experiments were carried out using Bruker AV-300, AVB-400, AVQ-400, AV-500, AV-600 MHz, or AV-900 MHz (equipped with a TCI cryoprobe) spectrometers at ambient temperatures (unless otherwise noted). $^1H$ and $^{13}C\{^1H\}$ NMR experiments were internally calibrated to residual solvents relative to tetramethylsilane. $^{19}F$ NMR was calibrated externally to hexafluorobenzene. Quantitative GC experiments were performed on an Agilent 7890 GC equipped with an HP-5 column (25 m x 0.20 mm x 0.33 μm film) and an FID detector. High resolution mass spectrometry (HRMS) experiments were carried out by the QB3/Chemistry Mass Spectrometry Facility at the University of California, Berkeley. ESIHR experiments were performed on a LTQ-FT instrument (from Thermo-Finnigan) with direct injection using Excalibur software. EIHR experiments were performed on an Autospec Premier instrument (from Waters) using MassLynx software.

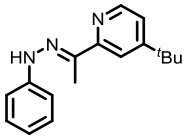
Elemental analyses were performed at the Microanalytical Laboratory at the University of California, Berkeley using a Perkin Elmer 2400 Series II combustion analyzer equipped for determination of %C, %H and %N (as well as %S). Single crystal X-ray diffraction experiments were performed at the CheXray crystallography facility at the University of California, Berkeley with a Bruker APEX-II CCD area detector using Mo Kα radiation (λ = 0.71073 Å) monochromated by QUAZAR multilayer mirrors. Crystals were kept at 100(2) K during data collection. Data collection was performed using Bruker APEX2 software. Unit cell refinement and data reduction were performed using Bruker SAINT software. Structures were solved in WinGX using SHELXT-2014 software and refined with SHELXL-2014 software using anisotropic parameters. All thermal ellipsoid graphics were rendered using ORTEP-32 software.

**Synthesis of Ligands and Pt(II) Complexes.**

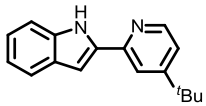
**Scheme S1. General N-N$^-$ Ligand Synthetic Route.**




**a:** $R^{4,5,6,7}$ = H, $R^{4'}$ = $^t$Bu
**b:** $R^{4,7}$ = F, $R^{5,6}$ = H, $R^{4'}$ = $^t$Bu
**c:** $R^{4,5,6,7}$ = F, $R^{4'}$ = $^t$Bu
**d:** $R^{4,6,7}$ = H, $R^5$ = H, $R^{4'}$ = H
**e:** $R^{4,6,7}$ = H, $R^5$ = OMe, $R^{4'}$ = H
**f:** $R^{4,6,7}$ = H, $R^5$ = Me, $R^{4'}$ = H
**g:** $R^{4,6,7}$ = H, $R^5$ = F, $R^{4'}$ = H
**h:** $R^{4,6,7}$ = H, $R^5$ = Cl, $R^{4'}$ = H
**i:** $R^{4,6,7}$ = H, $R^5$ = Br, $R^{4'}$ = H
**j:** $R^{4,5,6}$ = H, $R^7$ = Cl, $R^{4'}$ = H



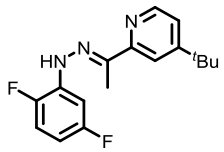
**Synthesis of (*E*)-4-(*tert*-butyl)-2-(1-(2-phenylhydrazono)ethyl)pyridine (S3a)**. Aryl hydryazine **S2a** (0.60 mL, 5.7 mmol, 1 equiv) and 4-*tert*-butyl-2-acetylpyridine (1.0 g, 5.7 mmol, 1 equiv) were dissolved in absolute ethanol (10 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) and refluxed at 90 °C for 4 h under air until judged complete by TLC (10% ethyl acetate/hexanes). Upon completion, the reaction mixture was cooled to ambient temperature and then diluted with water (50 mL). The crude mixture was extracted with dichloromethane (3 x 50 mL). The organic layers were combined, washed with brine (50 mL), dried over $Na_2SO_4$, and filtered. Volatile components were removed under reduced pressure yielding the title compound as an orange solid (1.3 g, 87 %). $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 8.44 (d, $J$ = 5.3 Hz, 1H), 8.19 (s, 1H, N–H), 7.63 (s, 1H), 7.30 (t, $J$ = 7.7 Hz, 2H), 7.22 (d, $J$ = 7.4 Hz, 3H), 6.90 (t, $J$ = 7.2 Hz, 1H), 2.38 (s, 3H, N=CCH$_3$), 1.37 (s, 9H, $^t$Bu). $^{13}$C{$^1$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 160.5, 156.5, 148.4, 143.4, 129.7, 120.8, 120.3, 116.8, 113.6, 112.9, 35.1, 30.7, 10.3. HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{17}H_{21}N_3$ 267.1735; Found 267.1729.



**Synthesis of 2-(4-(*tert*-butyl)pyridin-2-yl)-1*H*-indole (1a, $^t$BuPyInd)**. Hydrazone **S3a** (1.3 g, 4.9 mmol, 1 equiv) was heated to 140 °C in neat polyphosphoric acid (3 mL) under air for 1.5 h using a large stir bar to ensure thorough mixing. After completion, the reaction mixture was cooled to ambient temperature and quenched with $NaOH_{(aq)}$ (150 mL, 20 wt%). The crude

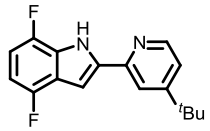
mixture was extracted with dichloromethane (4 x 50 mL). The organic layers were combined, washed with brine (50 mL), dried over $MgSO_4$, and filtered. Volatile components were removed under reduced pressure to afford an orange solid. Purification by $SiO_2$ column chromatography (eluting with 10% ethyl acetate/hexanes) afforded the title compound as an off-white powder (0.59 g, 48%). $^1$H NMR (benzene-$d_6$, 400.1 MHz): δ 9.57 (s, 1H), 8.42 (dd, $J$ = 5.3, 0.6 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.69 (dd, $J$ = 1.8, 0.6 Hz, 1H), 7.21 – 7.18 (m, 2H), 7.08 – 7.02 (m, 1H), 6.95 (dd, $J$ = 2.0, 0.8 Hz, 1H), 6.77 (dd, $J$ = 5.3, 1.9 Hz, 1H), 1.08 (s, 9H). $^1$H NMR (dichloromethane-$d_2$, 400.1 MHz): δ 9.83 (s, 1H, N–H), 8.48 (d, $J$ = 5.3 Hz, 1H), 7.82 (d, $J$ = 1.9 Hz, 1H), 7.64 (d, $J$ = 7.9 Hz, 1H), 7.43 (d, $J$ = 8.3 Hz, 1H), 7.23 – 7.16 (m, 2H), 7.09 (t, $J$ = 7.8 Hz, 1H), 7.05 (d, $J$ = 2.1 Hz, 1H), 1.38 (s, 9H, $^t$Bu). $^{13}$C{$^1$H} NMR (dichloromethane-$d_2$, 150.9 MHz): 161.3, 150.6, 149.4, 137.7, 136.9, 129.6, 123.3, 121.4, 120.4, 120.1, 117.1, 111.7, 100.2, 35.2, 30.7. HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{17}H_{18}N_2$ 250.1470; Found 250.1470.

**Synthesis of ($^t$BuPyInd)PtPh(SMe$_2$) (2a)**. C*is*-$(SMe_2)_2PtPh_2$ (200 mg, 0.42 mmol, 1.1 equiv) and **1a** (100 mg, 0.40 mmol, 1 equiv) were dissolved in benzene (20 mL). The reaction mixture was allowed to stir at ambient temperature for 5 h. Volatile components were then removed under reduced pressure. Under ambient atmosphere, $SiO_2$ column chromatography (eluting with 10% ethyl acetate/hexanes) provided the title compound as a yellow solid (220 mg, 95%). X-Ray quality crystals were obtained by slow diffusion of pentane into toluene at -35 °C. $^1$H NMR (benzene-$d_6$, 600.1 MHz): δ 8.31 (d, $J$ = 8.3 Hz, 1H), 8.03 (d, $J$ = 7.8 Hz, 1H), 7.74 (d with $^{195}$Pt satellites, $J_{HH}$ = 7.2 Hz, $J_{PtH}$ = 33 Hz, 2H), 7.67 (d, $J$ = 6.3 Hz, 1H), 7.55 (s, 1H), 7.45 (t, $J$ = 7.4 Hz, 1H), 7.33 (t, $J$ = 7.2 Hz, 1H), 7.27 – 7.17 (m, 3H), 7.15 – 7.12 (m, 1H), 5.83 (d, $J$ = 5.9 Hz, 1H), 1.54 (s with $^{195}$Pt satellites, $J_{PtH}$ = 53 Hz, 6H, $SMe_2$), 0.84 (s, 9H, $^t$Bu). $^1$H NMR (dichloromethane-$d_2$, 400.1 MHz): δ 7.88 (dd, $J$ = 8.3, 0.8 Hz, 1H), 7.78 (d, $J$ = 2.0 Hz, 1H), 7.62 – 7.56 (m, 3H), 7.53 (d, $J$ = 6.6 Hz, 1H), 7.10 (t, $J$ = 7.2 Hz, 2H), 7.05 – 6.97 (m, 3H), 6.89 (t, $J$ = 7.7 Hz, 1H), 6.80 (dd, $J$ = 6.4, 2.2 Hz, 1H), 2.31 (s with $^{195}$Pt satellites, $J_{PtH}$ = 56 Hz, 6H, $SMe_2$), 1.31 (s, 9H, $^t$Bu). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 150.9 MHz): δ 162.0, 160.0, 149.9, 148.6, 147.1, 146.8, 139.1, 138.0, 132.6, 123.7, 122.6, 122.3, 118.3, 118.1, 116.4, 115.1, 103.2, 34.7, 29.8, 22.9. Anal. Calcd for $C_{25}H_{28}N_2PtS$: C, 51.45; H, 4.84; N, 4.80; S, 5.49. Found: C, 51.13; H, 4.92; N, 4.55; S, 5.35.



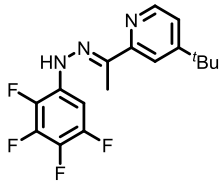

**Synthesis of (*E*)-4-(*tert*-butyl)-2-(1-(2-(2,5-difluorophenyl)hydrazono)ethyl) pyridine (S3b)**. Aryl hydrazine **S2b** (0.66 g, 4.5 mmol, 1.3 equiv) and 4-*tert*-butyl-2-acetylpyridine (0.64 g, 3.6 mmol, 1 equiv) were dissolved in absolute ethanol (10 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) and refluxed at 90 °C for 4 h under air until judged complete by TLC (10% ethyl acetate/hexanes). Upon completion, the reaction mixture was cooled to ambient temperature. Volatile components were removed under reduced pressure to afford an orange solid. Recrystallization from hexanes yielded the title compound as a yellow solid (0.88 g, 81%). $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 8.47 (dd, $J$ = 5.2, 0.6 Hz, 1H), 8.18 (d, $J$ = 1.3 Hz, 1H), 7.68 (s, 1H, N–H), 7.37 (ddd, $J$ = 10.0, 6.6, 3.1 Hz, 1H), 7.26 (dd, $J$ = 5.3, 1.9 Hz, 1H), 7.02

(ddd, $J$ = 11.1, 8.9, 4.9 Hz, 1H), 6.55 – 6.44 (m, 1H), 2.41 (s, 3H, N=CCH$_3$), 1.38 (s, 9H, $^t$Bu). $^{13}$C{$^1$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 161.2, 160.7, 159.6, 156.2, 148.9, 147.7, 147.0, 146.2, 135.2, 135.1, 135.0, 121.0, 117.2, 116.1, 116.0, 115.9, 105.8, 105.7, 105.6, 102.3, 102.1, 35.3, 30.9, 10.8 (fluorinated carbons difficult to observe and assign due to complicated C–F couplings). $^{19}$F NMR (dichloromethane-$d_2$, 376.4 MHz): δ -116.23 (br s), -141.45 (br s). HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{17}H_{19}N_3F_2$, 303.1547; Found, 303.1549.

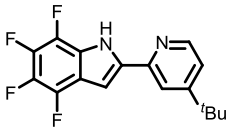



**Synthesis of 2-(4-(*tert*-butyl)pyridin-2-yl)-4,7-difluoro-1*H*-indole (1b, $^t$BuPyInd-4,5-F$_2$).** Hydrazone **S3b** (0.75 g, 2.5 mmol, 1 equiv) was heated to 110 °C in neat polyphosphoric acid (10 mL) for 4 h under air using a large stir bar to ensure thorough mixing. After completion, the reaction mixture was cooled to ambient temperature and quenched with NaOH$_{(aq)}$ (200 mL, 20 wt%). The crude mixture was extracted with diethyl ether (3 x 100 mL). The organic layers were combined, washed with brine (50 mL), dried over MgSO$_4$, and filtered. Volatile components were removed under reduced pressure to afford an orange/yellow solid. Purification by SiO$_2$ column chromatography (eluting with 10% ethyl acetate/hexanes) afforded the title compound as a yellow powder (0.11 g, 15%). $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 10.08 (s, 1H, N–H), 8.50 (d, $J$ = 5.3 Hz, 1H, Py), 7.85 (d, $J$ = 1.7 Hz, 1H, Py), 7.27 (dd, $J$ = 5.3, 1.8 Hz, 1H, Py), 7.17 – 7.09 (m, 1H, Ind), 6.82 (ddd, $J$ = 10.3, 8.7, 3.5 Hz, 1H, Ind), 6.67 (ddd, $J$ = 9.6, 8.6, 3.1 Hz, 1H, Ind), 1.38 (s, 9H, $^t$Bu). $^{13}$C{$^1$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 161.8, 153.8, 152.2, 149.7, 147.3, 145.7, 139.0, 127.1, 127.0, 126.9, 121.7, 121.6, 121.5, 120.9, 117.6, 107.8, 107.7, 107.6, 104.6, 104.5, 104.4, 104.3, 96.9, 35.4, 30.8 (fluorinated carbons difficult to observe and assign due to complicated C–F couplings). $^{19}$F NMR (dichloromethane-$d_2$, 376.4 MHz): δ -127.61 (dd, $J$ = 22.5, 9.5 Hz), -139.43 (dd, $J$ = 22.2, 10.3 Hz). HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{17}H_{16}N_2F_2$ 286.1282; Found, 286.1284.

**Synthesis of ($^t$BuPyInd-4,7-F$_2$)PtPh(SMe$_2$) (2b).** In a manner similar to that used above for **2a**, *cis*-(SMe$_2$)$_2$PtPh$_2$ (175 mg, 0.37 mmol, 1 equiv) and **1b** (110 mg, 0.39 mmol, 1.1 equiv) were dissolved in benzene (20 mL). Purification by SiO$_2$ column chromatography (eluting with 10% ethyl acetate/hexanes) yielded the title compound as a yellow solid (202 mg, 88%). X-Ray quality crystals were obtained by slow diffusion of pentane into toluene at -35 °C. $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 7.85 (d, $J$ = 1.5 Hz, 1H), 7.56 (d, $J$ = 7.2 Hz, 2H), 7.52 (d, $J$ = 6.3 Hz, 1H), 7.19 (d, $J$ = 2.6 Hz, 1H), 7.10 (t, $J$ = 7.4 Hz, 2H), 7.03 (t, $J$ = 7.3 Hz, 1H), 6.87 (dd, $J$ = 6.2, 1.9 Hz, 1H), 6.63 (ddd, $J$ = 12.2, 8.3, 3.9 Hz, 1H), 6.47 (td, $J$ = 9.2, 2.5 Hz, 1H), 2.18 (s with $^{195}$Pt satellites, $J_{PtH}$ = 58 Hz, 6H, SMe$_2$), 1.32 (s, 9H, $^t$Bu). $^{13}$C{$^1$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 163.8, 158.5, 154.6, 153.0, 152.9, 149.9, 149.8, 148.8, 148.5, 148.2, 148.1, 143.5, 137.5, 136.9, 136.8, 136.7, 136.76, 128.8, 124.0, 123.8, 123.7, 123.6, 123.5, 119.8, 117.5, 105.8, 105.7, 105.6, 101.04, 100.99, 100.90, 100.8, 99.0, 35.8, 30.4, 24.3 (fluorinated carbons difficult to observe and assign due to complicated C–F couplings). $^{19}$F NMR (dichloromethane-$d_2$, 376.4 MHz): δ -127.70 (ddd, $J$ = 23.3, 9.5, 4.0 Hz), -129.99 (dd, $J$ = 23.3, 12.3 Hz). Anal. Calcd for $C_{25}H_{26}F_2N_2PtS$: C, 48.46; H, 4.23; N, 4.52. Found: C, 48.66; H, 4.31; N, 4.50.



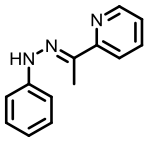
**Synthesis of (*E*)-4-(*tert*-butyl)-2-(1-(2-(2,3,4,5-tetrafluorophenyl)hydrazono)ethyl) pyridine (S3c).** Aryl hydrazine **S2c** (1.8 g, 9.7 mmol, 1.3 equiv) and 4-*tert*-butyl-2-acetylpyridine (1.4 g, 7.8 mmol, 1 equiv) were dissolved in absolute ethanol (40 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) and refluxed at 90 °C for 4 h under air until judged complete by TLC (10% ethyl acetate/hexanes). Upon completion, the reaction mixture was cooled to ambient temperature. Volatile components were removed under reduced pressure to afford an orange/yellow solid. Purification by $SiO_2$ column chromatography (eluting with 10% ethyl acetate/hexanes and then 50% ethyl acetate/hexanes) afforded the title compound as a yellow powder (1.6 g, 61%). $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 8.46 (d, $J$ = 5.7 Hz, 1H, Py), 8.11 (d, $J$ = 1.4 Hz, 1H, Py), 7.55 (s, 1H, N–H), 7.32 – 7.28 (m, 1H, $C_6F_4H$), 7.27 (dd, $J$ = 5.2, 1.9 Hz, 1H, Py), 2.41 (s, 3H, N=C$CH_3$), 1.37 (s, 9H, $^t$Bu). $^{13}$C{$^1$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 160.6, 155.7, 148.8, 148.2, 148.0, 141.3, 135.1, 132.9, 121.1, 117.0, 97.1, 96.9, 35.1, 30.7, 10.8 (fluorinated carbons difficult to observe and assign due to complicated C–F couplings). $^{19}$F NMR (dichloromethane-$d_2$, 376.4 MHz): -139.50 (dt, $J$ = 22.0, 11.0 Hz), -157.73 (t, $J$ = 20.3 Hz), -162.77 – -163.04 (m), -170.46 – -170.94 (m). HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{17}H_{17}N_3F_4$ 339.1539; Found 339.1358.



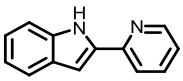
**Synthesis of 2-(4-(*tert*-butyl)pyridin-2-yl)-4,5,6,7-tetrafluoro-1*H*-indole (1c, $^t$BuPyInd-4,5,6,7-F$_4$).** Hydrazone **S3c** (1.0 g, 2.9 mmol, 1 equiv) was heated to 110 °C in neat polyphosphoric acid (7 mL) for 4 h under air using a large stir bar to ensure thorough mixing. After completion, the reaction mixture was cooled to ambient temperature and quenched with $NaOH_{(aq)}$ (150 mL, 10 wt%). The crude mixture was extracted with dichloromethane (4 x 50 mL). The organic layers were combined, washed with brine (100 mL), dried over $MgSO_4$, and filtered. Volatile components were removed under reduced pressure to afford an orange/yellow solid. Purification by $SiO_2$ column chromatography (eluting with 5% ethyl acetate/hexanes) afforded the title compound as a yellow powder (0.25 g, 27%). $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 10.08 (s, 1H, N–H), 8.50 (dd, $J$ = 5.3, 0.9 Hz, 1H, Py), 7.82 (dd, $J$ = 1.9, 0.9 Hz, 1H, Py), 7.29 (dd, $J$ = 5.3, 1.8 Hz, 1H, Py), 7.14 (d, $J$ = 2.7 Hz, 1H, Ind), 1.38 (s, 9H, $^t$Bu). $^{13}$C{$^1$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 161.3, 149.1, 148.5, 139.6, 138.9, 138.8, 137.9, 136.4, 136.3, 136.2, 136.0, 135.8, 134.4, 134.3, 134.2, 133.6, 133.5, 120.9, 120.5, 116.9, 115.4, 115.2, 96.1, 34.8, 30.1 (fluorinated carbons difficult to observe and assign due to complicated C–F couplings). $^{19}$F NMR (dichloromethane-$d_2$, 376.4 MHz): δ -150.12 (dd, $J$ = 19.6, 17.1 Hz), -160.95 (ddt, $J$ = 19.8, 16.7, 3.5 Hz), -165.11 (td, $J$ = 19.4, 1.7 Hz), -169.64 (td, $J$ = 19.7, 3.9 Hz). HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{17}H_{14}N_2F_4$ 322.1093; Found, 322.1093.

**Synthesis of ($^t$BuPyInd-4,5,6,7-F$_4$)PtPh(SMe$_2$) (2c).** In a manner similar to that used above for **2a**, *cis*-$(SMe_2)_2PtPh_2$ (121 mg, 0.26 mmol, 1.1 equiv) and **1c** (75 mg, 0.23 mmol, 1 equiv) were dissolved in benzene (20 mL). Purification by $SiO_2$ column chromatography (eluting with 10%

ethyl acetate/hexanes) yielded the title compound as a yellow solid (131 mg, 86%). X-Ray quality crystals were obtained by slow diffusion of pentane into toluene at -35 °C. $^{1}$H NMR (benzene-$d_6$, 600.1 MHz): δ 7.58 (d, $J$ = 7.4 Hz, 2H), 7.53 (d, $J$ = 6.3 Hz, 1H), 7.40 (s, 1H), 7.21 (s, 1H), 7.17-7.10 (m, 3H), 7.07 (t, $J$ = 7.1 Hz, 1H), 5.86 (d, $J$ = 5.8 Hz, 1H), 1.49 (s with $^{195}$Pt satellites, $J_{PtH}$ = 55 Hz, 6H, $SMe_2$), 0.80 (s, 9H, $^{t}$Bu). $^{13}$C{$^{1}$H} NMR (benzene-$d_6$, 150.9 MHz): δ 162.3, 157.9, 149.0, 148.9, 148.8, 148.2, 143.2, 137.0, 136.5, 136.4, 134.4, 134.3, 134.2, 132.8, 132.7, 132.6, 131.5, 131.4, 131.3, 123.6, 119.9, 118.7, 117.8, 117.7, 117.6, 117.6, 116.3, 99.3, 34.4, 29.3, 22.6. (fluorinated carbons difficult to observe and assign due to complicated couplings). $^{19}$F NMR (dichloromethane-$d_2$, 376.4 MHz): δ -151.69 (td, $J$ = 20.6, 18.6, 4.6 Hz), -153.35 (dd, $J$ = 20.8, 15.2 Hz), -169.26 (td, $J$ = 20.2, 3.9 Hz), -173.48 (td, $J$ = 20.1, 4.0 Hz). Anal. Calcd for $C_{25}H_{24}F_4N_2PtS$: C, 45.80; H, 3.69; N, 4.27; S, 4.89. Found: C, 45.99; H, 3.69; N, 4.08; S, 5.05.

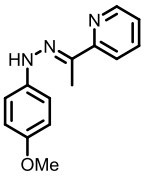



**Synthesis of (*E*)-2-(1-(2-phenylhydrazono)ethyl)pyridine (S3d).** A mixture of aryl hydrazine **S2a** (2.0 mL, 20 mmol, 1 equiv) and 2-acetylpyridine (2.3 mL, 20 mmol, 1 equiv) in absolute ethanol (20 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) was heated to 90 °C for 2 h under air until reaction was judged complete by TLC (10% ethyl acetate/hexanes). Upon completion, the reaction mixture was cooled to 0 °C, resulting in the formation of orange needles. The solution was filtered and the solid was washed with cold absolute ethanol. Residual volatile components were removed under reduced pressure to afford the title compound as orange needles (3.1 g, 73%). $^{1}$H NMR (dimethyl sulfoxide-$d_6$, 600.1 MHz): δ 9.49 (s, 1H, NH), 8.52 (d, $J$ = 4.7 Hz, 1H, Py), 8.11 (d, $J$ = 8.1 Hz, 1H, Py), 7.76 (td, $J$ = 7.7, 1.9 Hz, 1H, Py), 7.31 – 7.22 (m, 5H, $C_6H_5$), 6.80 (tt, $J$ = 7.2, 1.3 Hz, 1H, Py), 2.34 (s, 3H, N=C$CH_3$). $^{13}$C{$^{1}$H} NMR (dimethyl sulfoxide-$d_6$, 150.9 MHz): δ 156.2, 148.3, 145.5, 141.4, 136.1, 128.9, 122.2, 119.4, 119.2, 113.0, 11.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{14}N_3$ 212.1182; Found 212.1177.

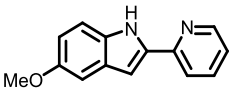



**Synthesis of 2-(pyridin-2-yl)-1*H*-indole (1d, PyInd)**. Hydrazone **S3d** (1.0 g, 4.7 mmol, 1 equiv) was heated to 140 °C in neat polyphosphoric acid (3 mL) for 2 h under air using a large stir bar to ensure thorough mixing. After completion, the reaction mixture was cooled to ambient temperature and quenched with $NaOH_{(aq)}$ (50 mL, 20 wt%). The crude mixture was extracted with dichloromethane (4 x 50 mL). The organic layers were combined, washed with brine (50 mL), dried over $MgSO_4$, and filtered. Volatile components were removed under reduced pressure to afford an orange solid. Purification by $SiO_2$ column chromatography (eluting with 10% ethyl acetate/hexanes) afforded the title compound as a yellow powder (0.32 g, 35%). $^{1}$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 9.68 (s, 1H, N–H), 8.58 (d, $J$ = 4.8 Hz, 1H), 7.83 (d, $J$ = 8.0 Hz, 1H), 7.75 (td, $J$ = 7.7, 1.8 Hz, 1H), 7.64 (d, $J$ = 7.9 Hz, 1H), 7.42 (d, $J$ = 8.2 Hz, 1H), 7.24 – 7.15 (m, 2H), 7.09 (t, $J$ = 7.5 Hz, 1H), 7.04 – 7.03 (m, 1H). $^{13}$C{$^{1}$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 150.7, 149.6, 137.2, 137.0, 136.9, 129.6, 123.5, 122.5, 121.5, 120.5, 120.2, 111.7, 100.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{11}N_2$ 195.0917; Found 195.0913.

**Synthesis of (PyInd)PtPh(SMe$_2$) (2d).** In a manner similar to that used above for **2a**, *cis*-(SMe$_2$)$_2$PtPh$_2$ (75 mg, 0.16 mmol, 1 equiv) and **1d** (39 mg, 0.20 mmol, 1.3 equiv) were dissolved in benzene (20 mL). The crude product was washed with 10% ethyl acetate/hexanes solution (20 mL) to afford the title compound as a yellow solid (81 mg, 97%). $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 7.88 (d, $J$ = 8.4 Hz, 1H), 7.81 (d, $J$ = 8.1 Hz, 1H), 7.71 (td, $J$ = 7.7, 1.6 Hz, 1H), 7.67 (dd, $J$ = 5.9, 1.3 Hz, 1H), 7.65 – 7.55 (m, 3H), 7.11 (t, $J$ = 7.4 Hz, 2H), 7.05 – 6.96 (m, 3H), 6.90 (ddd, $J$ = 7.9, 6.7, 1.0 Hz, 1H), 6.77 (ddd, $J$ = 7.3, 6.0, 1.6 Hz, 1H), 2.31 (s with $^{195}$Pt satellites, $J_{PtH}$ = 61 Hz, 6H, SMe$_2$). $^{13}$C{$^1$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 159.9, 149.3, 149.1, 147.9, 147.6, 138.6, 137.6, 134.6, 128.6, 123.8, 122.3, 121.7, 121.0, 120.4, 117.9, 114.7, 102.7, 23.8. Anal. Calcd for C$_{21}$H$_{20}$N$_2$PtS: C, 47.81; H, 3.82; N, 5.31. Found: C, 47.99; H, 3.56; N, 5.29.



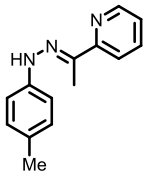

**Synthesis of (*E*)-2-(1-(2-(4-methoxyphenyl)hydrazono)ethyl)pyridine (S3e).** A mixture of aryl hydrazine **S2e** (as the HCl salt, 3.6 g, 20 mmol, 1 equiv) and 2-acetylpyridine (2.3 mL, 20 mmol, 1 equiv) in absolute ethanol (20 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) was heated to 90 °C for 3 h under air until reaction was judged complete by TLC (10% ethyl acetate/hexanes). Upon completion, the reaction mixture was cooled to 0 °C, resulting in the formation of an orange/red solid. The solution was filtered and the solid was washed with cold absolute ethanol. Residual volatile components were removed under reduced pressure to afford the title compound as a dark orange powder (4.2 g, 85%). $^1$H NMR (dimethyl sulfoxide-$d_6$, 600.1 MHz): δ 10.47 (s, 1H, N–H), 8.69 (d, $J$ = 5.6 Hz, 1H), 8.41 (t, $J$ = 7.7 Hz, 1H), 8.21 (d, $J$ = 8.3 Hz, 1H), 7.73 (t, $J$ = 6.5 Hz, 1H), 7.60 (d, $J$ = 8.8 Hz, 2H), 6.88 (d, $J$ = 8.9 Hz, 2H), 3.72 (s, 3H, OMe), 2.39 (s, 3H, N=CCH$_3$). $^{13}$C{$^1$H} NMR (dimethyl sulfoxide-$d_6$, 150.9 MHz): δ 154.4, 149.7, 144.9, 142.0, 137.9, 130.6, 123.2, 122.6, 115.7, 114.3, 55.2, 11.9. HRMS (EI) m/z: [M]$^+$ Calcd for C$_{14}$H$_{15}$N$_3$O 241.1215; Found 241.1212.



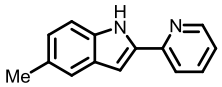

**Synthesis of 5-methoxy-2-(pyridin-2-yl)-1*H*-indole (1e, PyInd-5-MeO).** Hydrazone **S3e** (0.70 g, 2.9 mmol, 1 equiv) was dissolved in glacial acetic acid (10 mL). The reaction mixture was heated to 115 °C under a flow of $N_2$ for 28 h, after which the reaction mixture was cooled to ambient temperature. The reaction mixture was quenched with KOH$_{(aq)}$ (100 mL, 20 wt%). The crude mixture was extracted with dichloromethane (3 x 50 mL). The organic layers were combined, washed with brine, dried over MgSO$_4$, and filtered. The crude mixture was purified by SiO$_2$ column chromatography (eluting with 50% chloroform/toluene and then chloroform) to afford the title compound as a yellow solid (0.084 g, 13%). $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 9.65 (s, 1H, N–H), 8.57 (dt, $J$ = 4.9, 1.3 Hz, 1H), 7.80 (dt, $J$ = 8.1, 1.1 Hz, 1H), 7.74 (td, $J$ = 7.7, 1.8 Hz, 1H), 7.29 (d, $J$ = 8.8 Hz, 1H), 7.18 (ddd, $J$ = 7.4, 4.8, 1.2 Hz, 1H), 7.09 (d, $J$ = 2.4 Hz, 1H), 6.96 (dd, $J$ = 2.0, 0.9 Hz, 1H), 6.85 (dd, $J$ = 8.8, 2.4 Hz, 1H), 3.84 (s, 3H, OMe). $^{13}$C{$^1$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 154.9, 150.7, 149.6, 137.8, 137.0, 132.2,

130.0, 122.4, 120.1, 114.1, 112.5, 102.6, 100.5, 56.0. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{12}N_2O$ 224.0950; Found 224.0951.

**Synthesis of (PyInd-5-MeO)PtPh(SMe$_2$) (2e)**. C*is*-$(SMe_2)_2PtPh_2$ (40 mg, 0.08 mmol, 1 equiv) and **1e** (19 mg, 0.08 mmol, 1 equiv) were dissolved in benzene (20 mL). The reaction mixture was allowed to stir at 50 °C for 20 h. Volatile components were then removed under reduced pressure. The crude product was triturated with 10% ethyl acetate/hexanes solution (20 mL) to afford the title compound as a yellow solid (36 mg, 77%). $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 7.77 (d, $J$ = 9.0 Hz, 1H), 7.75 (d, $J$ = 8.6 Hz, 1H), 7.68 (ddd, $J$ = 8.5, 5.8, 1.5 Hz, 1H), 7.64 (d, $J$ = 6.0 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.10 (t, $J$ = 7.5 Hz, 2H), 7.05 – 7.01 (m, 1H), 7.00 (d, $J$ = 2.6 Hz, 1H), 6.93 (s, 1H), 6.74 (ddd, $J$ = 7.4, 6.0, 1.6 Hz, 1H), 6.69 (dd, $J$ = 8.9, 2.6 Hz, 1H), 3.82 (s, 3H, OMe), 2.30 (s with $^{195}$Pt satellites, $J_{PtH}$ = 58 Hz, 6H, $SMe_2$). $^{13}C\{^1H\}$ NMR (dichloromethane-$d_2$, 150.9 MHz): δ 153.1, 149.2, 147.0, 146.9, 146.6, 145.8, 138.5, 137.5, 137.0, 128.5, 123.7, 120.6, 120.2, 115.5, 113.9, 102.2, 101.5, 55.8, 23.7. Anal. Calcd for $C_{22}H_{22}N_2OPtS \cdot 0.5\ CD_2Cl_2$: C, 44.96; H, 4.02; N, 4.66. Found: C, 45.15; H, 3.74; N, 4.40.



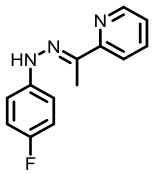

**Synthesis of *(E)*-2-(1-(2-(*p*-tolyl)hydrazono)ethyl)pyridine (S3f).** A mixture of aryl hydrazine **S2f** (as the HCl salt, 2.2 g, 14 mmol, 1 equiv) and 2-acetylpyridine (1.6 mL, 14 mmol, 1 equiv) in absolute ethanol (30 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) was heated to 90 °C for 2 h under air until reaction was judged complete by TLC (10% ethyl acetate/hexanes). Upon completion, the reaction mixture was cooled to 0 °C, resulting in the formation of an orange solid. The solution was filtered and the solid was washed with cold absolute ethanol. Residual volatile components were removed under reduced pressure to afford the title compound as an orange powder (2.5 g, 78%). $^1$H NMR (dimethyl sulfoxide-$d_6$, 600.1 MHz): δ 10.26 (s, 1H, N–H), 8.67 (d, $J$ = 5.6 Hz, 1H), 8.37 (t, $J$ = 8.1 Hz, 1H), 8.23 (d, $J$ = 8.2 Hz, 1H), 7.71 (t, $J$ = 6.6 Hz, 1H), 7.45 (d, $J$ = 8.0 Hz, 2H), 7.11 (d, $J$ = 8.0 Hz, 2H), 2.37 (s, 3H, N=C$CH_3$), 2.25 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (dimethyl sulfoxide-$d_6$, 150.9 MHz): δ 149.9, 144.7, 142.4, 141.9, 131.8, 130.1, 129.4, 123.4, 122.7, 114.4, 20.4, 11.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}N_3$ 226.1339; Found 226.1334.



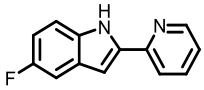

**Synthesis of 5-methyl-2-(pyridin-2-yl)-1*H*-indole (1f, PyInd-5-Me)**. Hydrazone **S3f** (1.0 g, 4.4 mmol, 1 equiv) was heated to 140 °C in neat polyphosphoric acid (3 mL) for 1 h under air using a large stir bar to ensure thorough mixing. After completion, the reaction mixture was cooled to ambient temperature and quenched with $NaOH_{(aq)}$ (150 mL, 10 wt%). The crude mixture was extracted with dichloromethane (4 x 50 mL). The organic layers were combined, washed with brine (50 mL), dried over $MgSO_4$, and filtered. Volatile components were removed under

reduced pressure to afford an orange solid. Purification by $SiO_2$ column chromatography (eluting with 10% ethyl acetate/hexanes) afforded the title compound as a white powder (0.31 g, 33%). $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 9.49 (s, 1H, N–H), 8.56 (dt, $J$ = 5.0, 1.4 Hz, 1H), 7.80 (dt, $J$ = 8.3, 1.2 Hz, 1H), 7.73 (td, $J$ = 7.7, 1.8 Hz, 1H), 7.42 (s, 1H), 7.32 (d, $J$ = 8.3 Hz, 1H), 7.18 (ddd, $J$ = 7.4, 4.9, 1.3 Hz, 1H), 7.04 (d, $J$ = 8.3 Hz, 1H), 6.94 (d, $J$ = 1.8 Hz, 1H), 2.43 (s, 3H, Me). $^{13}$C{$^1$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 150.8, 149.6, 137.3, 137.0, 135.3, 129.9, 129.8, 125.3, 122.3, 121.0, 120.1, 111.4, 100.2, 21.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}N_2$ 209.1073; Found 209.1069.

**Synthesis of (PyInd-5-Me)PtPh(SMe$_2$) (2f).** In a manner similar to that used above for **2a**, *cis*-$(SMe_2)_2PtPh_2$ (75 mg, 0.16 mmol, 1 equiv) and **1f** (42 mg, 0.20 mmol, 1.3 equiv) were dissolved in benzene (10 mL). The crude product was triturated with 10% ethyl acetate/hexanes solution (20 mL) to afford the title compound as a yellow solid (75 mg, 88%). $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 7.76 (dd, $J$ = 8.9, 2.2 Hz, 2H), 7.72 – 7.64 (m, 2H), 7.60 (d with $^{195}$Pt satellites, $J_{HH}$ = 6.7 Hz, $J_{PtH}$ = 31, 2H), 7.35 (s, 1H), 7.11 (t, $J$ = 7.5 Hz, 2H), 7.02 (td, $J$ = 7.2, 1.5 Hz, 1H), 6.92 (s, 1H), 6.86 (dd, $J$ = 8.4, 1.8 Hz, 1H), 6.73 (ddd, $J$ = 7.2, 5.8, 1.5 Hz, 1H), 2.38 (s, 3H, Me), 2.30 (s with $^{195}$Pt satellites, $J_{PtH}$ = 59 Hz, 6H, $SMe_2$). $^{13}$C{$^1$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 159.9, 149.2, 147.6, 146.3, 146.0, 138.5, 137.6, 132.2, 128.6, 126.9, 124.5, 123.8, 121.0, 120.7, 120.3, 114.4, 102.2, 23.8, 21.7. Anal. Calcd for $C_{22}H_{22}N_2PtS$: C, 48.79; H, 4.09; N, 5.17. Found: C, 49.07; H, 3.89; N, 4.80.

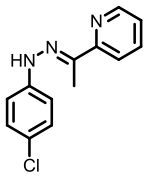



**Synthesis of (*E*)-2-(1-(2-(4-fluorophenyl)hydrazono)ethyl)pyridine (S3g).** A mixture of aryl hydrazine **S2g** (as the HCl salt, 2.0 g, 12 mmol, 1 equiv) and 2-acetylpyridine (1.4 mL, 12 mmol, 1 equiv) in absolute ethanol (30 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) was heated to 90 °C for 3 h under air until reaction was judged complete by TLC (10% ethyl acetate/hexanes). Upon completion, the reaction mixture was cooled to 0 °C, resulting in the formation of an orange/yellow solid. The solution was filtered and the solid was washed with cold absolute ethanol. Residual volatile components were removed under reduced pressure to afford the title compound as a yellow powder (2.7 g, 83%). $^1$H NMR (dimethyl sulfoxide-$d_6$, 600.1 MHz): δ 10.48 (s, 1H, N–H), 8.71 (d, $J$ = 5.3 Hz, 1H), 8.41 (t, $J$ = 8.3 Hz, 1H), 8.25 (d, $J$ = 8.3 Hz, 1H), 7.75 (t, $J$ = 6.6 Hz, 1H), 7.63 (dd, $J$ = 8.8, 4.7 Hz, 2H), 7.13 (t, $J$ = 8.9 Hz, 2H), 2.40 (s, 3H, N=C$CH_3$). $^{13}$C{$^1$H} NMR (dimethyl sulfoxide-$d_6$, 150.9 MHz): δ 158.1, 156.5, 149.9, 144.5, 142.8, 140.8, 132.9, 123.7, 122.7, 115.6, 115.5, 115.4, 12.0 (fluorinated carbons difficult to observe and assign due to complicated C–F couplings). $^{19}$F NMR (dimethyl sulfoxide-$d_6$, 376.4 MHz, DMSO): δ -122.5 (br s). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{13}N_3F$ 230.1088; Found 230.1084.



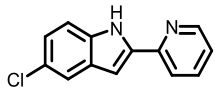
**Synthesis of 5-fluoro-2-(pyridin-2-yl)-1*H*-indole (1g, PyInd-5-F)**. Hydrazone **S3g** (1.0 g, 4.4 mmol, 1 equiv) was heated to 140 °C in neat polyphosphoric acid (3 mL) for 1.5 h under air using a large stir bar to ensure thorough mixing. After completion, the reaction mixture was cooled to ambient temperature and quenched with $NaOH_{(aq)}$ (150 mL, 10 wt%). The crude mixture was extracted with dichloromethane (4 x 50 mL). The organic layers were combined, washed with brine (50 mL), dried over $MgSO_4$, and filtered. Volatile components were removed under reduced pressure to afford a tan solid. Purification by $SiO_2$ column chromatography (eluting with 10% ethyl acetate/hexanes) afforded the title compound as a white powder (0.58 g, 62%). $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 9.73 (s, 1H, N–H), 8.59 (d, $J$ = 4.7 Hz, 1H), 7.82 (d, $J$ = 7.9 Hz, 1H), 7.76 (td, $J$ = 7.8, 1.8 Hz, 1H), 7.35 (dd, $J$ = 8.8, 4.4 Hz, 1H), 7.29 (dd, $J$ = 9.7, 2.5 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.00 (d, $J$ = 2.1 Hz, 1H), 6.96 (td, $J$ = 9.1, 2.5 Hz, 1H). $^{13}$C{$^1$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 158.8, 157.2, 149.8, 149.2, 138.5, 136.7, 133.0, 129.4, 129.3, 122.3, 119.8, 112.1, 112.0, 111.4, 111.2, 105.5, 105.3, 100.2, 100.1 (fluorinated carbons difficult to observe and assign due to complicated C–F couplings). $^{19}$F NMR (dichloromethane-$d_2$, 376.4 MHz): δ -124.2 (br s). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{10}N_2F$ 213.0823; Found 213.0817.

**Synthesis of (PyInd-5-F)PtPh(SMe$_2$) (2g).** In a manner similar to that used above for **2a**, *cis*-$(SMe_2)_2PtPh_2$ (75 mg, 0.16 mmol, 1 equiv) and **1g** (42 mg, 0.20 mmol, 1.3 equiv) were dissolved in benzene (10 mL). The crude product was triturated with hexanes (10 mL) then 10% ethyl acetate/hexanes solution (15 mL) to afford the title compound as a yellow solid (63 mg, 73%). $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 7.84 (dd, $J$ = 9.1, 4.8 Hz, 1H), 7.80 (d, $J$ = 8.0 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.67 (d, $J$ = 5.9 Hz, 1H), 7.59 (d with $^{195}$Pt satellites, $J_{HH}$ = 6.9 Hz, $J_{PtH}$ = 37, 2H), 7.20 (dd, $J$ = 10.2, 2.7 Hz, 1H), 7.11 (t, $J$ = 7.4 Hz, 2H), 7.03 (t, $J$ = 7.4 Hz, 1H), 6.98 (s, 1H), 6.82 – 6.75 (m, 2H), 2.31 (s with $^{195}$Pt satellites, $J_{PtH}$ = 60 Hz, 6H, $SMe_2$). $^{13}$C{$^1$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 159.5, 157.8, 156.3, 149.3, 147.9, 145.8, 145.3, 138.7, 137.5, 128.6, 123.9, 121.3, 120.5, 115.4, 111.0, 110.8, 105.1, 104.9, 102.5, 102.4, 23.7 (fluorinated carbons difficult to observe and assign due to complicated C–F couplings). $^{19}$F NMR (dichloromethane-$d_2$, 376.4 MHz): δ -127.04 (td, $J$ = 9.6, 4.7 Hz). Anal. Calcd for $C_{21}H_{19}FN_2PtS$: C, 46.24; H, 3.51; N, 5.14. Found: C, 46.50; H, 3.45; N, 4.99.



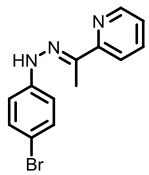

**Synthesis of (*E*)-2-(1-(2-(4-chlorophenyl)hydrazono)ethyl)pyridine (S3h).** A mixture of aryl hydrazine **S2h** (as the HCl salt, 3.6 g, 20 mmol, 1 equiv) and 2-acetylpyridine (2.3 mL, 20 mmol, 1 equiv) in absolute ethanol (20 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) was heated to 90 °C for 2 h under air until the reaction was judged complete by TLC (10% ethyl acetate/hexanes). Upon completion, the reaction mixture was cooled to 0 °C, resulting in the formation of an orange solid. The solution was filtered and the solid was washed with cold absolute ethanol. Residual volatile components were removed under reduced pressure to afford the title compound as a light orange powder (3.9 g, 77%). $^1$H NMR (dimethyl sulfoxide-$d_6$, 600.1

MHz): δ 10.69 (s, 1H, N–H), 8.75 (d, $J$ = 5.2 Hz, 1H), 8.44 (t, $J$ = 7.4 Hz, 1H), 8.26 (d, $J$ = 8.2 Hz, 1H), 7.79 (t, $J$ = 6.3 Hz, 1H), 7.69 (d, $J$ = 8.7 Hz, 2H), 7.29 (d, $J$ = 8.8 Hz, 2H), 2.43 (s, 3H, N=CCH$_3$). $^{13}$C{$^1$H} NMR (dimethyl sulfoxide-$d_6$, 150.9 MHz): δ 149.6, 144.7, 143.2, 142.6, 133.6, 128.6, 124.6, 123.9, 122.9, 115.9, 12.3. HRMS (EI) m/z: [M]$^+$ Calcd for $C_{13}H_{12}N_3Cl$ 245.0720; Found 245.0720.



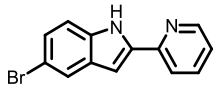
**Synthesis of 5-chloro-2-(pyridin-2-yl)-1*H*-indole (1h, PyInd-5-Cl)**. Hydrazone **S3h** (1.0 g, 4.1 mmol, 1 equiv) was heated to 140 °C in neat polyphosphoric acid (3 mL) for 1.5 h under air using a large stir bar to ensure thorough mixing. After completion, the reaction mixture was cooled to ambient temperature and quenched with $NaOH_{(aq)}$ (100 mL, 10 wt%). The crude mixture was extracted with dichloromethane (4 x 50 mL). The organic layers were combined, washed with brine (50 mL), dried over $MgSO_4$, and filtered. Volatile components were removed under reduced pressure to afford a yellow solid. Purification by $SiO_2$ column chromatography (eluting with 10% ethyl acetate/hexanes and then 30% ethyl acetate/hexanes) afforded the title compound as a white powder (0.49 g, 52%). $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 9.97 (s, 1H, N–H), 8.59 (d, $J$ = 4.7 Hz, 1H), 7.82 (d, $J$ = 7.9 Hz, 1H), 7.76 (td, $J$ = 7.7, 1.8 Hz, 1H), 7.61 (d, $J$ = 2.2 Hz, 1H), 7.32 (d, $J$ = 8.6 Hz, 1H), 7.23 (dd, $J$ = 7.4, 4.9 Hz, 1H), 7.15 (dd, $J$ = 8.7, 2.0 Hz, 1H), 6.98 (d, $J$ = 2.3 Hz, 1H). $^{13}$C{$^1$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 150.2, 149.7, 138.7, 137.2, 135.3, 130.6, 125.9, 123.6, 122.9, 120.7, 120.4, 112.9, 100.2. HRMS (EI) m/z: [M]$^+$ Calcd for $C_{13}H_9N_2Cl$ 228.0454; Found 228.0455.

**Synthesis of (PyInd-5-Cl)PtPh(SMe$_2$) (2h).** In a manner similar to that used above for **2a**, *cis*-(SMe$_2$)$_2$PtPh$_2$ (45 mg, 0.10 mmol, 1 equiv) and **1h** (27 mg, 0.12 mmol, 1.2 equiv) were dissolved in benzene (10 mL). The crude product was triturated with 10% ethyl acetate/hexanes solution (15 mL) to afford the title compound as a yellow solid (50 mg, 94%). $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 7.85 (d, $J$ = 8.9 Hz, 1H), 7.81 (dd, $J$ = 7.7, 1.4 Hz, 1H), 7.73 (td, $J$ = 7.7, 1.6 Hz, 1H), 7.68 (d, $J$ = 5.7 Hz, 1H), 7.59 (d with $^{195}$Pt satellites, $J_{HH}$ = 6.8 Hz, $J_{PtH}$ = 36 Hz, 2H), 7.54 (d, $J$ = 2.2 Hz, 1H), 7.15 – 7.09 (m, 2H), 7.05 – 7.00 (m, 1H), 6.97 (s, 1H), 6.95 (dd, $J$ = 8.9, 2.1 Hz, 1H), 6.81 (ddd, $J$ = 7.5, 5.9, 1.5 Hz, 1H), 2.30 (s with $^{195}$Pt satellites, $J_{PtH}$ = 60 Hz, 6H, SMe$_2$). $^{13}$C{$^1$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 159.3, 149.4, 147.8, 147.3, 145.2, 138.8, 137.4, 132.7, 128.7, 123.9, 123.2, 122.4, 121.5, 120.6, 120.5, 115.8, 102.0, 23.7. Anal. Calcd for $C_{21}H_{19}ClN_2PtS \cdot 1.2CD_2Cl_2$: C, 40.02; H, 3.60; N, 4.20. Found: C, 40.01; H, 3.60; N, 4.22.



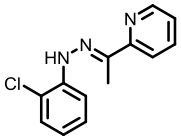
**Synthesis of (*E*)-2-(1-(2-(4-bromophenyl)hydrazono)ethyl)pyridine (S3i).** A mixture of aryl hydrazine **S2i** (as the HCl salt, 3.2 g, 14 mmol, 1 equiv) and 2-acetylpyridine (1.6 mL, 14 mmol, 1 equiv) in absolute ethanol (30 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) was heated to 90 °C for 2 h under air until reaction was judged complete by TLC (10% ethyl

acetate/hexanes). Upon completion, the reaction mixture was cooled to 0 °C, resulting in the formation of a light orange solid. The solution was filtered and the solid was washed with cold absolute ethanol. Residual volatile components were removed under reduced pressure to afford the title compound as an orange powder (3.6 g, 87%). $^{1}$H NMR (dimethyl sulfoxide-$d_6$, 600.1 MHz): δ 10.59 (s, 1H, N–H), 8.74 (d, $J$ = 5.0 Hz, 1H), 8.42 (t, $J$ = 7.0 Hz, 1H), 8.26 (d, $J$ = 6.7 Hz, 1H), 7.78 (t, $J$ = 5.3 Hz, 1H), 7.60 (d, $J$ = 6.0 Hz, 2H), 7.43 (d, $J$ = 6.4 Hz, 2H), 2.42 (s, 3H, N=CCH$_3$). $^{13}$C{$^{1}$H} NMR (dimethyl sulfoxide-$d_6$, 150.9 MHz): δ 148.7, 148.5, 144.6, 143.6, 142.9, 131.5, 123.9, 122.9, 116.3, 112.4, 12.2. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{13}H_{13}N_3Br$ 290.0287; Found 290.0286.

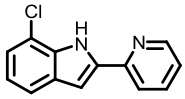



**Synthesis of 5-bromo-2-(pyridin-2-yl)-1*H*-indole (1i, PyInd-5-Br)**. Hydrazone **S3i** (1.0 g, 3.5 mmol, 1 equiv) was heated to 140 °C in neat polyphosphoric acid (3 mL) for 1.5 h under air using a large stir bar to ensure thorough mixing. After completion, the reaction mixture was cooled to ambient temperature and quenched with $KOH_{(aq)}$ (100 mL, 20 wt%). The crude mixture was extracted with dichloromethane (4 x 50 mL). The organic layers were combined, washed with brine (50 mL), dried over $MgSO_4$, and filtered. Volatile components were removed under reduced pressure to afford an orange oily solid. Purification by $SiO_2$ column chromatography (eluting with 10% ethyl acetate/hexanes) afforded an oily white solid. Recrystallization from hexanes layered onto a benzene solution afforded the title compound as a white solid (0.19 g, 20%). $^{1}$H NMR (benzene-$d_6$, 600.1 MHz): δ 9.42 (s, 1H, N–H), 8.30 (d, $J$ = 4.6 Hz, 1H), 7.85 – 7.74 (m, 1H), 7.25 (dd, $J$ = 8.6, 1.9 Hz, 1H), 7.22 (d, $J$ = 7.9 Hz, 1H), 7.01 (td, $J$ = 7.7, 1.7 Hz, 1H), 6.61 (d, $J$ = 8.6 Hz, 1H), 6.57 (d, $J$ = 1.6 Hz, 1H), 6.55 (dd, $J$ = 7.5, 4.8 Hz, 1H). $^{13}$C{$^{1}$H} NMR (benzene-$d_6$, 150.9 MHz): δ 150.3, 149.2, 138.1, 136.4, 135.5, 131.4, 126.4, 124.0, 122.1, 120.0, 113.8, 113.3, 100.4. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{13}H_{10}N_2Br$ 273.0022; Found 273.0018.

**Synthesis of (PyInd-5-Br)PtPh(SMe$_2$) (2i).** In a manner similar to that used above for **2a**, *cis*-(SMe$_2$)$_2$PtPh$_2$ (63 mg, 0.13 mmol, 1 equiv) and **1i** (36 mg, 0.13 mmol, 1 equiv) were dissolved in benzene (10 mL). The crude product was triturated with 10% ethyl acetate/hexanes solution (15 mL) to afford the title compound as a yellow solid (60 mg, 75%). $^{1}$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 7.82 – 7.79 (m, 2H), 7.74 (td, $J$ = 7.7, 1.5 Hz, 1H), 7.70 (d, $J$ = 2.1 Hz, 1H), 7.68 (dd, $J$ = 6.1, 1.3 Hz, 1H), 7.59 (dd with $^{195}$Pt satellites, $J_{HH}$ = 7.7, 1.4 Hz, $J_{PtH}$ = 31 Hz, 2H), 7.11 (t, $J$ = 7.6 Hz, 2H), 7.07 (dd, $J$ = 8.9, 2.1 Hz, 1H), 7.03 (tt, $J$ = 7.3, 1.2 Hz, 1H), 6.97 (d, $J$ = 1.0 Hz, 1H), 6.82 (ddd, $J$ = 7.4, 6.0, 1.5 Hz, 1H), 2.30 (s with $^{195}$Pt satellites, $J_{PtH}$ = 59 Hz, 6H, SMe$_2$). $^{13}$C{$^{1}$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 159.3, 149.4, 147.6, 147.4, 138.8, 137.4, 133.5, 128.6, 124.8, 123.9, 123.7, 121.5, 120.7, 120.6, 116.2, 110.9, 101.9, 23.7. Anal. Calcd for $C_{21}H_{19}BrN_2PtS \bullet 0.7CD_2Cl_2$: C, 39.06; H, 3.29; N, 4.20. Found: C, 39.24; H, 3.02; N, 4.09.



**Synthesis of (*E*)-2-(1-(2-(2-chlorophenyl)hydrazono)ethyl)pyridine (S3j).** A mixture of aryl hydrazine **S2j** (as the HCl salt, 3.1 g, 20 mmol, 1 equiv) and 2-acetylpyridine (2.3 mL, 20 mmol, 1 equiv) in absolute ethanol (20 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) was heated to 90 °C for 2 h under air until reaction was judged complete by TLC (10% ethyl acetate/hexanes). Upon completion, the reaction mixture was cooled to 0 °C, resulting in the formation of a light yellow solid. The solution was filtered and the solid was washed with cold absolute ethanol. Residual volatile components were removed under reduced pressure to afford the title compound as a light yellow powder (3.8 g, 77%). $^{1}$H NMR (dimethyl sulfoxide-$d_6$, 600.1 MHz): δ 8.90 (s, 1H, N–H), 8.74 (d, $J$ = 5.4 Hz, 1H), 8.34 – 8.28 (m, 2H), 7.98 (d, $J$ = 8.3 Hz, 1H), 7.73 (t, $J$ = 7.0 Hz, 1H), 7.44 (d, $J$ = 8.0 Hz, 1H), 7.35 (t, $J$ = 7.8 Hz, 1H), 6.98 (t, $J$ = 7.7 Hz, 1H), 2.46 (s, 3H, N=CCH$_3$). $^{13}$C{$^{1}$H} NMR (dimethyl sulfoxide-$d_6$, 150.9 MHz): δ 144.5, 140.1, 129.3, 128.1, 124.3, 123.1, 122.8, 122.3, 122.1, 118.5, 117.6, 116.4, 11.2. HRMS (EI) m/z: [M]$^+$ Calcd for $C_{13}H_{12}N_3Cl$ 245.0720; Found 245.0717.



**Synthesis of 7-chloro-2-(pyridin-2-yl)-1*H*-indole (1j, PyInd-7-Cl)**. Hydrazone **S3j** (1.0 g, 4.1 mmol, 1 equiv) was heated to 140 °C in neat polyphosphoric acid (3 mL) for 1.5 h under air using a large stir bar to ensure thorough mixing. After completion, the reaction mixture was cooled to ambient temperature and quenched with KOH$_{(aq)}$ (100 mL, 20 wt%). The crude mixture was extracted with dichloromethane (4 x 50 mL). The organic layers were combined, washed with brine (50 mL), dried over $MgSO_4$, and filtered. Volatile components were removed under reduced pressure to afford an orange solid. Purification by $SiO_2$ column chromatography (eluting with 10% ethyl acetate/hexanes) afforded the title compound as a white powder (0.18 g, 19%). $^{1}$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 9.74 (s, 1H, N–H), 8.61 (d, $J$ = 4.7 Hz, 1H), 7.81 (d, $J$ = 7.9 Hz, 1H), 7.75 (td, $J$ = 7.8, 1.8 Hz, 1H), 7.57 (d, $J$ = 7.9 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.10 – 7.00 (m, 2H). $^{13}$C{$^{1}$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 150.1, 149.7, 138.1, 137.1, 134.2, 131.0, 122.9, 122.7, 121.3, 120.3, 120.2, 117.1, 101.5. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{13}H_{10}N_2Cl$ 229.0527; Found 229.0527.

**Synthesis of (PyInd-7-Cl)PtPh(SMe$_2$) (2j).** C*is*-(SMe$_2$)$_2$PtPh$_2$ (40 mg, 0.08 mmol, 1 equiv) and **1j** (23 mg, 0.10 mmol, 1.2 equiv) were dissolved in benzene (10 mL). The reaction mixture was stirred at 50 °C for 22 h. Volatile components were removed under reduced pressure. The crude product was triturated with 25% ethyl acetate/hexanes solution (15 mL) to afford the title compound as a yellow solid (23 mg, 49%). $^{1}$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 7.80 (d, $J$ = 8.6 Hz, 1H), 7.75 (td, $J$ = 7.7, 1.5 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.52 (ddd, $J$ = 8.0, 3.2, 1.2 Hz, 2H), 7.13 (s, 1H), 7.10 – 7.04 (m, 3H), 7.03 – 6.98 (m, 1H), 6.86 (t, $J$ = 7.6 Hz, 1H), 6.82 (ddd, $J$ = 7.4, 5.9, 1.6 Hz, 1H), 2.15 (s with $^{195}$Pt satellites, $J_{PtH}$ = 62 Hz, 6H, SMe$_2$). $^{13}$C{$^{1}$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 160.9, 159.5, 149.6, 149.1, 139.2, 138.8, 137.7, 134.4, 128.6, 124.0, 123.0, 121.5, 120.8, 120.7, 120.4, 118.9, 103.7, 24.6. Anal. Calcd for $C_{21}H_{19}ClN_2PtS$: C, 44.88; H, 3.41; N, 4.98. Found: C, 44.85; H, 3.37; N, 4.67.

**Synthesis of (PyInd)PtPh(SEt$_2$) (2k).** [(μ-SEt$_2$)PtPh$_2$]$_2$ (45 mg, 0.05 mmol, 1 equiv) and **1d** (42 mg, 0.10 mmol, 2 equiv) were dissolved in benzene (10 mL). The reaction mixture was stirred at 50 °C for 20 h. Volatile components were removed under reduced pressure. The crude product was triturated with hexanes (10 mL) then 15% ethyl acetate/hexanes solution (15 mL) to afford the title compound as a yellow solid (41 mg, 72%). $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 8.11 (d, $J$ = 8.5 Hz, 1H), 7.81 (d, $J$ = 8.1 Hz, 1H), 7.70 (td, $J$ = 7.7, 1.6 Hz, 1H), 7.66 – 7.55 (m, 4H), 7.10 (t, $J$ = 7.5 Hz, 2H), 7.03 (s, 1H), 7.03 – 6.98 (m, 2H), 6.89 (t, $J$ = 7.4 Hz, 1H), 6.75 (ddd, $J$ = 7.3, 5.9, 1.6 Hz, 1H), 2.75 (dq with $^{195}$Pt satellites, $J_{HH}$ = 14.8, 7.6 Hz, $J_{PtH}$ = 60 Hz, 2H, S**C**$\underline{\mathbf{H_2}}$CH$_3$), 2.55 (dq with $^{195}$Pt satellites, $J_{HH}$ = 14.1, 7.4 Hz, $J_{PtH}$ = 71 Hz, 2H, S**C**$\underline{\mathbf{H_2}}$CH$_3$), 1.43 (t, $J$ = 7.4 Hz, 6H, SCH$_2$$\underline{\mathbf{CH_3}}$).$^{13}$C{$^1$H} NMR (dichloromethane-$d_2$, 150.9 MHz): δ 160.8, 150.3, 150.0, 147.5, 145.9, 139.5, 138.5, 133.0, 129.5, 124.6, 123.0, 122.5, 121.8, 121.4, 118.8, 116.5, 103.6, 32.6, 14.2. Anal Calcd for $C_{23}H_{24}N_2PtS$ • 0.4 $CD_2Cl_2$: C, 47.61; H, 4.37; N, 4.75. Found: C, 47.85; H, 4.02; N, 4.71.

**Synthesis of ($^t$BuPyInd)PtPh(C$_2$H$_4$) (3) *via* Ligand Exchange with 2a.** Inside a glovebox, **2a** (30 mg, 0.05 mmol) was dissolved in benzene-$d_6$ (0.7 mL) in a low pressure/vacuum J. Young NMR tube (4 mm outer diameter, 3 mL). On a Schlenk line, the solution was thoroughly degassed by three freeze/pump/thaw cycles after which ethylene (1 atm) was added at ambient temperature. After 1 day at ambient temperature, the volatile components were removed under reduced pressureto remove SMe$_2$ in order to prevent back reactions. Inside a glovebox, fresh benzene-$d_6$ was added and degassed as described previously. Additional ethylene (1 atm) was added and the mixture was left for 1 day. This process was repeated a total of four times. The reaction mixture was concentrated under reduced pressure and passed through a SiO$_2$ column under ambient atmosphere (eluting with 5% ethyl acetate/hexanes and then 10% ethyl acetate/hexanes) to yield the title compound as a yellow solid (8 mg, 29%). Recrystallization by slow diffusion of pentane into a toluene solution of **3** yielded X-ray quality crystals. $^1$H NMR (benzene-$d_6$, 600.1 MHz): δ 7.76 (t, $J$ = 6.4 Hz, 1H), 7.69 (t, $J$ = 6.5 Hz, 1H), 7.56 – 7.43 (m, 2H), 7.31 – 7.22 (m, 3H), 7.10 – 7.02 (m, 2H), 6.94 (d, $J$ = 5.1 Hz, 1H), 6.76 (t, $J$ = 5.7 Hz, 1H), 6.45 (t, $J$ = 6.8 Hz, 1H), 6.31 (dt, $J$ = 5.9, 2.9 Hz, 1H), 3.40 (s with $^{195}$Pt satellites, $J_{PtH}$ = 59 Hz, 4H, C$_2$H$_4$), 0.99 (s, 9H, $^t$Bu). $^1$H NMR (dichloromethane-$d_2$, 400.1 MHz): δ 7.87 (d, $J$ = 1.7 Hz, 1H), 7.69 (d, $J$ = 6.0 Hz, 1H), 7.55 – 7.40 (m, 3H), 7.23 (dd, $J$ = 6.0, 2.0 Hz, 1H), 7.15 – 7.04 (m, 3H), 7.01 (d, $J$ = 0.8 Hz, 1H), 6.78 (tt, $J$ = 7.5, 0.9 Hz, 1H), 6.56 (ddd, $J$ = 8.3, 6.9, 1.3 Hz, 1H), 5.64 (dd, $J$ = 8.6, 0.7 Hz, 1H), 3.83 (s with $^{195}$Pt satellites, $J_{PtH}$ = 59 Hz, 4H, C$_2$H$_4$), 1.39 (s, 9H, $^t$Bu). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 150.9 MHz): δ 162.1, 157.5, 153.9, 148.8, 147.8, 142.2, 139.1, 137.7, 128.9, 124.6, 124.0, 121.0, 120.0, 118.8, 117.5, 116.3, 104.0, 63.9, 34.8, 29.9. Anal. Calcd for $C_{25}H_{26}N_2Pt$: C, 54.64; H, 4.77; N, 5.10. Found: C, 54.98; H, 4.54; N, 5.09.

**Synthesis of ($^t$BuPyInd)PtPh(C$_2$H$_4$) (3) *via* Ligation and Phenylation of Zeise's Dimer.** A mixture of Zeise's dimer (91 mg, 0.15 mmol, 1 equiv), **1a** (77 mg, 0.31 mmol, 2 equiv), and NaO$^t$Bu (35 mg, 0.31 mmol, 2 equiv) were dissolved in benzene (20 mL). A bright orange solid rapidly precipitated from solution. The mixture was stirred for 16 h at ambient temperature. Volatile components were removed under reduced pressure. Recrystallization from hexanes afforded *cis*/*trans*-(PyInd)PtCl(C$_2$H$_4$) as an orange solid (114 mg, 72%) which was identified by $^1$H NMR spectroscopy and used without further purification. $^1$H NMR (dichloromethane-$d_2$,

300.1 MHz): δ 8.60 (d, $J$ = 8.5 Hz, 1H), 7.78 (d, $J$ = 2.3 Hz, 1H), 7.56 (d, $J$ = 8.1 Hz, 1H), 7.41 (d, $J$ = 6.6 Hz, 1H), 7.19 – 7.06 (m, 2H), 7.04 – 6.93 (m, 2H), 4.67 – 4.36 (m, 2H, $C_2H_4$), 4.42 – 3.97 (m, 2H, $C_2H_4$), 1.38 (s, 9H, $^t$Bu).

In THF (10 mL), *cis*/*trans*-(PyInd)PtCl($C_2H_4$) (114 mg, 0.22 mmol, 1 equiv) was treated with AgOTf (60 mg, 0.24 mmol, 1.1 equiv) at ambient temperature and stirred for 1 h. A solution of PhLi in THF (5 mL, 0.24 mmol, 47 mM, 1.1 equiv) was slowly added. The reaction mixture was then heated to 50 °C for 20 h in the dark. The reaction mixture was filtered over Celite and the filtrate was concentrated under reduced pressure. Purification by $SiO_2$ column chromatography (eluting with 5% ethyl acetate/hexanes) afforded the title compound as a yellow solid (25 mg, 20% yield). $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): δ 7.87 (d, $J$ = 1.9 Hz, 1H), 7.69 (d, $J$ = 6.2 Hz, 1H), 7.55 – 7.40 (m, 3H), 7.24 (dd, $J$ = 6.0, 2.1 Hz, 1H), 7.15 – 7.05 (m, 3H), 7.01 (d, $J$ = 0.9 Hz, 1H), 6.78 (td, $J$ = 7.5, 1.0 Hz, 1H), 6.56 (ddd, $J$ = 8.3, 6.9, 1.3 Hz, 1H), 5.64 (dd, $J$ = 8.6, 1.1 Hz, 1H), 3.84 (s with $^{195}$Pt satellites, $J_{PtH}$ = 60 Hz, 4H, $C_2H_4$), 1.39 (s, 9H, $^t$Bu).

**Synthesis of ($^t$BuPyInd)Pt($CH_2CH_2Ph$)($C_2H_4$) (4)**. *Caution: working with high pressures is a potential safety hazard, and the reaction vessel should be tested above working pressures prior to usage*. Inside a glovebox, **2a** (140 mg, 0.24 mmol) was dissolved in benzene (10 mL) in a 50 mL Teflon stoppered Schlenk flask equipped with a stir bar. On a Schlenk line, the solution was thoroughly degassed by three freeze/pump/thaw cycles, then ethylene was added while the reaction flask was still cool (ca. 10 °C, 1 atm). The reaction vessel was heated to 40 °C for 5 days. Volatile components were removed under reduced pressure to prevent back reactions. The reaction vessel was brought back into a glovebox and fresh benzene (10 mL) was added. Outside the glovebox, the solution was degassed and ethylene (> 1 atm) was added as described above. The reaction vessel was then heated to 40 °C for an additional 5 days. Volatile components were removed under reduced pressure, and purification by $SiO_2$ column chromatography (eluting with 5% ethyl acetate/hexanes and then 10% ethyl acetate/hexanes) yielded the title compound as a yellow solid (30 mg, 22%). X-Ray quality crystals were obtained by slow diffusion of pentane into toluene at -35 °C. $^1$H NMR (benzene-$d_6$, 600.1 MHz): δ 8.36 (d, $J$ = 8.5 Hz, 1H), 7.90 (d, $J$ = 7.8 Hz, 1H), 7.52 (d, $J$ = 1.7 Hz, 1H), 7.45 (d, $J$ = 7.3 Hz, 2H), 7.40 (t, $J$ = 7.7 Hz, 1H), 7.27 (t, $J$ = 7.7 Hz, 3H), 7.19 – 7.11 (m, 1H), 7.02 (s, 1H), 6.76 (d, $J$ = 5.9 Hz, 1H), 6.29 (dd, $J$ = 5.9, 1.9 Hz, 1H), 3.21 (t, $J$ = 8.1 Hz, 2H, PtCH$_2$**CH$_2$**Ph), 3.00 (s with $^{195}$Pt satellites, $J_{PtH}$ = 54 Hz, 4H, $C_2H_4$), 2.10 (t with $^{195}$Pt satellites, $J_{HH}$ = 8.2 Hz, $J_{PtH}$ = 67 Hz, 2H, Pt**CH$_2$**CH$_2$Ph), 0.97 (s, 9H, $^t$Bu). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 150.9 MHz): δ 161.7, 157.1, 149.9, 147.7, 146.0, 141.8, 132.3, 128.9, 128.7, 128.4, 125.7, 124.2, 121.6, 119.9, 119.1, 116.5, 116.4, 104.0, 60.2, 39.1, 34.8, 29.9. Anal. Calcd for $C_{27}H_{30}N_2Pt$: C, 56.14; H, 5.24; N 4.85. Found: C, 56.05; H, 5.41; N, 4.83.

## Catalytic Methods

**General Procedure for Ethylene Hydroarylation with Benzene-$d_6$ Using Catalysts 2a-k, 3, and 4**. Inside a glovebox, catalysts **2a-k**, **3**, or **4** (0.0026 mmol, 3.7 mM), benzene-$d_6$ (0.7 mL), and a known amount of Si(SiMe$_3$)$_4$ as an internal standard, were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. On a Schlenk line, the solution was thoroughly degassed by three freeze/pump/thaw cycles and ethylene (1 atm) was added at ambient temperature. The reaction vessel was submerged in a 100 °C bath. Product formation was monitored over a 24 h by $^1$H NMR spectroscopy after 50, 100, 150, 200, 250, 300, 1370 min of heating. Product formation was determined by identifying new benzylic and methyl resonances in the $^1$H NMR spectrum and comparing them to literature values.[6] Overall TON was

determined by comparing the benzylic peak to the internal standard peak. Selected $^1$H NMR resonances for benzylic/methyl protons for $C_6D_5C\underline{\mathbf{H_2}}C\underline{\mathbf{H_2}}D$: $^1$H NMR (benzene-$d_6$, 400.1 MHz): δ 2.44 (tt, $J_{HH}$ = 7.5 Hz, $J_{HD}$ = 1.1 Hz, 2H), 1.06 (tt, $J_{HH}$ = 7.5 Hz, $J_{HD}$ = 2.0 Hz, 2H). Polyethylbenzene formation was qualitatively identified by GC-MS after filtering through $Al_2O_3$ (Figure S16).

**High Pressure Ethylene Hydroarylation with Benzene Using Catalyst 2a**. *Caution: working with high pressures is a potential safety hazard, and the reaction vessel should be tested above working pressures prior to usage*. In a glovebox, a Fischer-Porter apparatus (50 mL) equipped with a stir bar was charged with catalyst **2a** (4.5 mg, 7.7 μmol, 3.7 mM) in benzene-$d_6$ (2.1 mL) with a known amount $Si(SiMe_3)_4$ as an internal standard. The apparatus was transferred onto a Schlenk line and attached to a high pressure ethylene inlet. The reaction vessel was then purged with ethylene, pressurized to 3 atm, and then heated to 100 °C with vigorous stirring for 6 h. After this time, the reaction vessel was depressurized and cooled to ambient temperature. A $^1$H NMR spectrum of the reaction mixture was acquired to determine ethylbenzene turnovers.

**Propylene Hydroarylation with Benzene-$d_6$ Using Catalysts 2a-k**. In a similar manner to that described in the general procedure above, catalysts **2a-k** (0.0026 mmol, 3.7 mM), benzene-$d_6$ (0.7 mL), propylene (1 atm), and a known amount of $Si(SiMe_3)_4$ as an internal standard were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath. Product formation was monitored over a 24 h period by $^1$H NMR spectroscopy after 50, 100, 150, 200, 250, 300, 1370 min of heating. Product formation was determined by identifying new benzylic and methyl resonances in the $^1$H NMR spectrum and comparing them to literature values of cumene-$d_6$ ($C_6D_5CHCH_3CH_2D$)[7] and *n*-propylbenzene-$d_6$ ($C_6D_5CH_2CHDCH_3$)[8]. For product selectivity ratios, the ratio of the benzylic peaks for the two isomers was calculated by $^1$H NMR spectroscopy. Overall TON was determined by comparing the benzylic peak to the internal standard peak for $Si(SiMe_3)_4$. Selected $^1$H NMR resonance for the benzylic proton for cumene-$d_6$ ($C_6D_5C\underline{\mathbf{H}}(CH_3)(CH_2D)$): $^1$H NMR (benzene-$d_6$, 400.1 MHz): δ 2.70 (h, $J_{HH}$ = 6.6 Hz, $J_{HD}$ = 1.3 Hz). Selected $^1$H NMR peak for the benzylic protons for *n*-propylbenzene-$d_6$ ($C_6D_5C\underline{\mathbf{H_2}}CHDCH_3$): $^1$H NMR (benzene-$d_6$, 400.1 MHz): δ 2.42 (dt, $J_{HH}$ = 7.3 Hz, $J_{HD}$ = 1.0 Hz).

**Hydroarylation of *tert*-Butylethylene with Benzene-$d_6$ Using Catalyst 2a.** Inside a glovebox, catalyst **2a** (0.0026 mmol, 0.3 mol% catalyst loading relative to olefin, 3.7 mM), benzene-$d_6$ (0.7 mL), *tert*-butylethylene (100 μL, 0.78 mmol), and a known amount of $Si(SiMe_3)_4$ as an internal standard, were heated to 100 °C for 24 h. A $^1$H NMR spectrum was acquired and new benzylic peaks were identified for *tert*-butylethylbenzene and 1-*tert*-butyl-1-phenylethane. These peaks were in agreement with literature values.[9] The overall TON was determined by comparing the integration of the benzylic peaks to the standard peak, and product selectivity was determined as the ratio of the two new benzylic peaks. Selected $^1$H NMR resonances for the benzylic protons for *tert*-butylethylbenzene and 1-*tert*-butyl-1-phenylethane: $^1$H NMR (300.1 MHz): δ 2.46 (dt, $J_{HH}$ = 9.2 Hz, $J_{HD}$ = 1.4 Hz), 2.41 (tt, $J_{HH}$ = 6.3 Hz, $J_{HD}$ = 1.3 Hz).

**Attempted Hydroarylation of Cyclohexene with Benzene-$d_6$ Using Catalyst 2a.** The general procedure was followed with **2a** (0.0026 mmol, 0.3 mol% catalyst loading relative to olefin, 3.7 mM), benzene-$d_6$ (0.7 mL), cyclohexene (8.0 μL, 0.082 mmol), and a known amount of

$Si(SiMe_3)_4$ as a standard were heated to 100 °C for 24 h. A $^1H$ NMR spectrum was acquired. No new products were identified and cyclohexene was not consumed.

**Attempted Hydroarylation of 1-Octene with Benzene-$d_6$ Using Catalyst 2a.** Catalyst **2a** (0.0026 mmol, 0.3 mol% catalyst loading relative to olefin, 3.7 mM), benzene-$d_6$ (0.7 mL), 1-octene (100 μL, 0.64 mmol), and a known amount of $Si(SiMe_3)_4$ as a standard were heated to 100 °C for 24 h. A $^1H$ NMR spectrum indicated only isomerization to 2-octene. No other products were identified.

**Ethylene Hydroarylation with Benzene Using Catalyst 2a**. In a similar manner to that described in the general procedure above, catalyst **2a** (1.5 mg, 0.0026 mmol, 3.7 mM), benzene (0.7 mL), ethylene (1 atm), and a known amount of $Si(SiMe_3)_4$ as a standard were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath for 24 h. The reaction mixture was then cooled to ambient temperature and an aliquot of the reaction mixture was diluted in chloroform-$d_1$. Product formation was determined by identifying new benzylic and methyl resonances in the $^1H$ NMR spectrum and comparing them to known literature values in chloroform-$d_1$.[10] TON was determined by comparing the benzylic peak to the internal standard peak. Selected $^1H$ NMR resonances for benzylic/methyl protons for $C_6H_5C\underline{\mathbf{H_2}}C\underline{\mathbf{H_3}}$: $^1H$ NMR (chloroform-$d_1$, 400.1 MHz): δ 2.65 (q, $J$ = 7.6 Hz, 2H), 1.22 (t, $J$ = 7.6, 3H).

**Competitive Ethylene Hydroarylation with Equimolar Benzene and Benzene-$d_6$ Using Catalyst 2a**. In a similar manner to that described in the general procedure above, catalyst **2a** (1.5 mg, 0.0026 mmol, 3.3 mM), benzene (0.4 mL), benzene-$d_6$ (0.4 mL), ethylene (1 atm), and a known amount of $Si(SiMe_3)_4$ as a standard were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath for 24 h. The ratio of $C_6H_5CH_2CH_3$ to $C_6D_5CH_2CH_2D$ was determined by $^1H$ and $^{13}C\{^1H\}$ NMR spectroscopy (Figure S15). In the $^1H$ NMR spectrum, the ratio was calculated by integration of the benzylic proton resonances. In $^{13}C\{^1H\}$ NMR spectrum, the ratio was calculated by integration of the methyl $CH_3$ and $CH_2D$ resonances [selected NMR value for mixture of $C_6D_5CH_2\mathbf{C}H_3$ and $C_6D_5CH_2\mathbf{C}H_2D$: $^{13}C\{^1H\}$ NMR (benzene-$d_6$, 226.4 MHz, $D_1$ = 60.0 s, temp = 298.0 K): δ 15.9 (s, measure $T_1$ = 3.9 s), 15.5 (t, $J_{CD}$ = 19.2 Hz, measured $T_1$ = 4.3 s)].[11]

**Hydroarylation of Ethylene with Toluene Using Catalyst 2a.** Inside a glove box, catalyst **2a** (0.0026 mmol, 3.7 mM), toluene (0.7 mL) and tridecane as an internal standard (7 μL, 0.029 mmol) were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. On a Schlenk line, the solution was thoroughly degassed by three freeze/pump/thaw cycles and then ethylene (1 atm) was added at ambient temperature. The reaction vessel was submerged in a 100 °C bath for 24 h. GC calibration curves and response factors were generated for authentic samples of *o*-ethyltoluene, *m*-ethyltoluene, and *p*-ethyltoluene versus a tridecane standard using known concentrations in ethyl acetate. The signals corresponding to *m*- and *p*-ethyltoluene could not be resolved and were integrated as a single peak. A 300 μL aliquot of the reaction mixture was dissolved in 1.5 mL ethyl acetate and filtered over a short plug of $Al_2O_3$ to remove any residual metal complexes. Using the response factor, this sample was then analyzed by GC to determine overall TON and product selectivity for *o*-ethyltoluene versus the mixture of *m*- and *p*-ethyltoluene.

**Ethylene Hydroarylation with Mesitylene Using Catalyst 2a**. In a similar manner to that described in the general procedure above, catalyst **2a** (0.0026 mmol, 3.7 mM), mesitylene (0.7 mL), ethylene (1 atm), and a known amount of $Si(SiMe_3)_4$ were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath for 24 h. The reaction mixture was cooled to ambient temperature and an aliquot was diluted in chloroform-$d_1$. Product formation was determined by identifying new benzylic and methyl resonances in the $^1$H NMR spectrum and comparing them to known literature values of 1-ethyl-2,4,6-trimethylbenzene.[12] Overall TON was determined by comparing the benzylic peak to the internal standard peak for $Si(SiMe_3)_4$. Selected $^1$H NMR resonances for benzylic/methyl protons for 1-ethyl-2,4,6-trimethylbenzene: $^1$H NMR (chloroform-$d_1$, 400.1 MHz): δ 2.60 (q, $J$ = 7.4 Hz, 2H), 2.29 (s, 6H), 2.25 (s, 3H), 1.08 (t, $J$ = 7.6 Hz, 3H).

**Ethylene Hydroarylation with Benzene-$d_6$ Using 2a with Added Base.** In a similar manner to that described in the general procedure above, catalyst **2a** (0.0026 mmol, 3.7 mM), benzene-$d_6$ (0.7 mL), 2,6-di-*tert*-butyl-4-methylpyridine (11 mg, 0.054 mmol, 20 equiv relative to **2a**), ethylene (1 atm) and a known amount of $Si(SiMe_3)_4$ as an internal standard were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath. Product formation was monitored over a 24 h period by $^1$H NMR spectroscopy after 50, 100, 150, 200, 250, 300, 1370 min of heating.

**Ethylene Hydroarylation with Benzene-$d_6$ Using Catalyst 2a or 4 with Added Dimethyl Sulfide**. In a similar manner to that described in the general procedure above, **2a** or **4** (0.0026 mmol, 3.7 mM), benzene-$d_6$ (0.7 mL), dimethyl sulfide (2.0 μL, 0.026 mmol, 10 equiv. relative to [Pt]), ethylene (1 atm), and a known amount of a $Si(SiMe_3)_4$ internal standard were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath. Product formation was monitored over a 24 h period by $^1$H NMR spectroscopy after 50, 100, 150, 200, 250, 300, 1370 min of heating.

**Ethylene Hydroarylation with Benzene-$d_6$ Using Catalysts 2a or 3 in the Presence of Hg(0).** In a similar manner to that described in the general procedure above, catalyst **2a** or **3** (0.0026 mmol, 3.7 mM), benzene-$d_6$ (0.7 mL), ethylene (1 atm), a known amount of $Si(SiMe_3)_4$ as an internal standard, and Hg(0) (ca. 1 pipette drop) were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction mixture was submerged in a 100 °C bath. Product formation was monitored over a 24 h period by $^1$H NMR spectroscopy after 50, 100, 150, 200, 250, 300, 1370 min of heating.

**Ethylene Hydroarylation with Benzene-$d_6$ Using Catalysts 2a or 3, Pre-Stirring with Hg(0).** In a glovebox, catalyst **2a** or **3** (0.0026 mmol, 3.7 mM) and a known amount $Si(SiMe_3)_4$ as a standard were dissolved in benzene-$d_6$ (0.7 mL). This solution was stirred at ambient temperature with Hg(0) (ca. 1 pipette drop) for 30 min. The solution was decanted and then filtered over Celite to remove residual Hg(0) from the reaction mixture. This solution was then added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. On a Schlenk line, the solution was thoroughly degassed by three freeze/pump/thaw cycles and then ethylene (1 atm) was added at ambient temperature. The reaction vessel was submerged in a 100 °C bath. Product

formation was monitored over a 24 h period by $^1$H NMR spectroscopy after 50, 100, 150, 200, 250, 300, 1370 min of heating.

**Thermolysis Reactions using Compounds 2a, 3 or 4 in Benzene-$d_6$.** Inside a glovebox, **2a**, **3**, or **4** (0.0086 mmol, 8.6 mM) and a known amount of $Si(SiMe_3)_4$ as an internal standard were dissolved in benzene-$d_6$ (1 mL) and added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath for 48 h. The reaction mixture was monitored by $^1$H NMR spectroscopy after 50, 100, 1370, 2810 min of heating.

**Thermolysis of 2a in Benzene-$d_6$ in the Presence of Hg(0).** In a glovebox, catalyst **2a** (0.0026 mmol, 3.7 mM), benzene-$d_6$ (0.7 mL), a known amount of $Si(SiMe_3)_4$ as a standard, and Hg(0) (ca. 1 pipette drop) were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath. Product formation was monitored over a 24 h period by $^1$H NMR spectroscopy after 50, 100, 150, 200, 250, 300, 1370 min of heating.

**Variable Temperature $^1$H NMR Spectroscopy with Compounds 2a, 3 or 4**. In a similar manner to that described in the general procedure above, catalysts **2a**, **3** or **4** (0.0026 mmol, 3.7 mM), benzene-$d_6$ (0.7 mL), ethylene (1 atm), and a known amount of $Si(SiMe_3)_4$ as a standard were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. An NMR spectrometer (500.2 MHz) was preheated to 80 °C. The temperature was separately calibrated using the peak-to-peak separation of resonances in neat ethylene glycol (measured temp = 353 K). Once the spectrometer reached temperature, the J. Young reaction vessel was injected into the spectrometer. Scans were taken every 10 min over a 3 h time span. Products were quantified versus the internal standard. The identity of Pt based species was identified versus authentic samples (*vide supra*).

**Styrene Determination in Ethylene Hydroarylation with Benzene Using Catalyst 2a**. In a similar manner to that described in the general procedure above, catalyst **2a** (1.5 mg, 0.0026 mmol, 3.7 mM), benzene-$d_6$ (0.7 mL), ethylene (1 atm), and a known amount of $Si(SiMe_3)_4$ as a standard were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath for 24 h. The reaction mixture was then cooled to ambient temperature and degassed by three freeze/pump/thaw cycles. Vinylic resonances for styrene,[13] *β*-(*E*)-deuterostyrene,[14] and *β*-(*Z*)-deuterostyrene[14] were identified in the $^1$H NMR spectrum and were in agreement with reported literature values. Products were quantified versus the internal standard. Selected $^1$H NMR resonances for the vinylic protons in styrene (PhC**H**=C**H$_2$**): $^1$H NMR (benzene-$d_6$, 400.1 MHz): δ 6.57 (dd, $J$ = 18.3, 11.0 Hz), 5.59 (dd, $J$ = 17.6, 1.3 Hz), 5.06 (dd, $J$ = 10.9, 1.2 Hz). Selected $^1$H NMR resonances for the vinylic protons in *β*-(*E*)-deuterostyrene (PhC**H**=C**H**D: $^1$H NMR (benzene-$d_6$, 400.1 MHz): δ 6.64 (bd, $J$ = 17.9 Hz), 5.69 (bd, $J$ = 17.9 Hz). Selected $^1$H NMR resonances for the vinylic protons in *β*-(*Z*)-deuterostyrene: $^1$H NMR (benzene-$d_6$, 400.1 MHz): 6.67 (bd, $J$ = 10.5 Hz), 5.16 (bd, $J$ = 10.9 Hz).

**Determination of Decomposition Products and Organometallic Speciation in Ethylene Hydroarylation with Benzene Using Catalyst 2a**. In a glovebox, catalyst **2a** (21 mg, 0.036

mmol, 7.2 mM) was dissolved in benzene (5 mL) in a 100 mL Teflon stoppered Schlenk flask equipped with a stir bar. On a Schlenk line, the solution was thoroughly degassed by three freeze/pump/thaw cycles and then ethylene (1 atm) was added at ambient temperature. The reaction mixture was heated to 100 °C for 20 h. The reaction mixture was then cooled to ambient temperature and volatile components were removed under reduced pressure. Dichloromethane was added to the residue. The resultant solution was spotted onto a preparatory $SiO_2$ TLC plate (eluting with 10% ethyl acetate/hexanes) in order to separate Pt(0) from organometallic and ligand species. Two broad bands ($R_f$ = 0.40-0.55, and 0.02-0.10) were observed. The top band was physically removed and the products were extracted with dichloromethane (2 x 10 mL). The solution was filtered to remove residual $SiO_2$. An aliquot of the resultant solution was filtered over $Al_2O_3$ and a HRMS (ESI-TOF) was acquired. The results are summarized in Table S1.

**EXPERIMENTAL FIGURES**

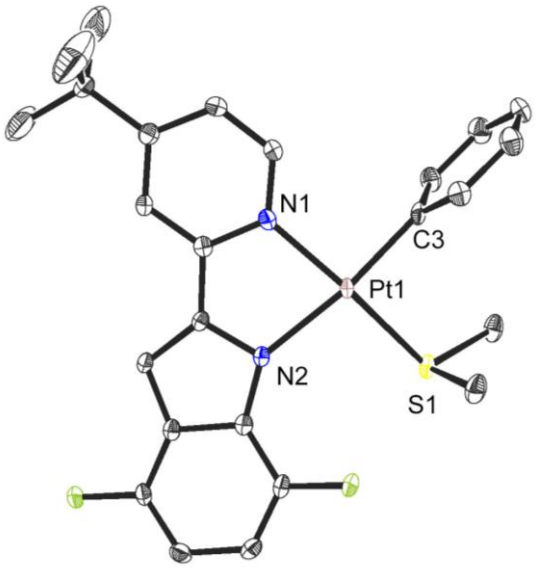



**Figure S1.** Crystal structure of **2b**, with thermal ellipsoid at 50% probability. For clarity, hydrogen atoms have been omitted. Selected bond length (Å) and angles (°) for **2**: C(3)–Pt(1): 2.009(3), N(1)–Pt(1): 2.049(2), N(2)–Pt(1): 2.125(2), S(1)–Pt(1): 2.2611(7), C(3)–Pt(1)–N(1): 93.16(10), C(3)–Pt(1)–S(1): 90.10(8), N(1)–Pt(1)-N(2): 79.19(9), N(2)–Pt(1)–S(1): 97.56(6).

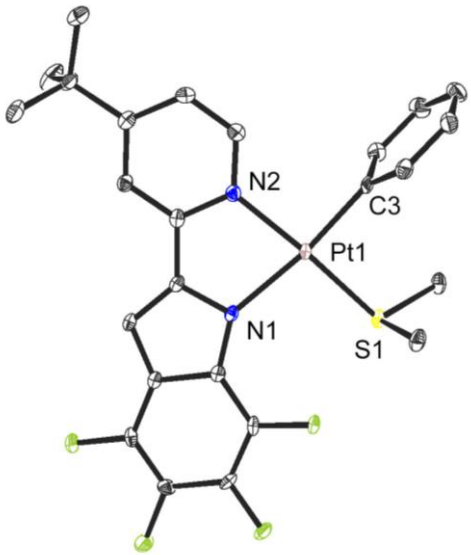



**Figure S2.** Crystal structure of **2c**, with thermal ellipsoid at 50% probability. For clarity, hydrogen atoms have been omitted. Selected bond length (Å) and angles (°) for **3**: C(3)–Pt(1): 2.008(2), N(2)–Pt(1): 2.0522(17), N(1)–Pt(1): 2.1244(16), S(1)–Pt(1): 2.2619(5), C(3)–Pt(1)–

N(2): 93.64(7), C(3)–Pt(1)–S(1): 89.83(6), N(2)–Pt(1)–N(1): 79.16(6), N(1)–Pt(1)–S(1): 97.36(5).

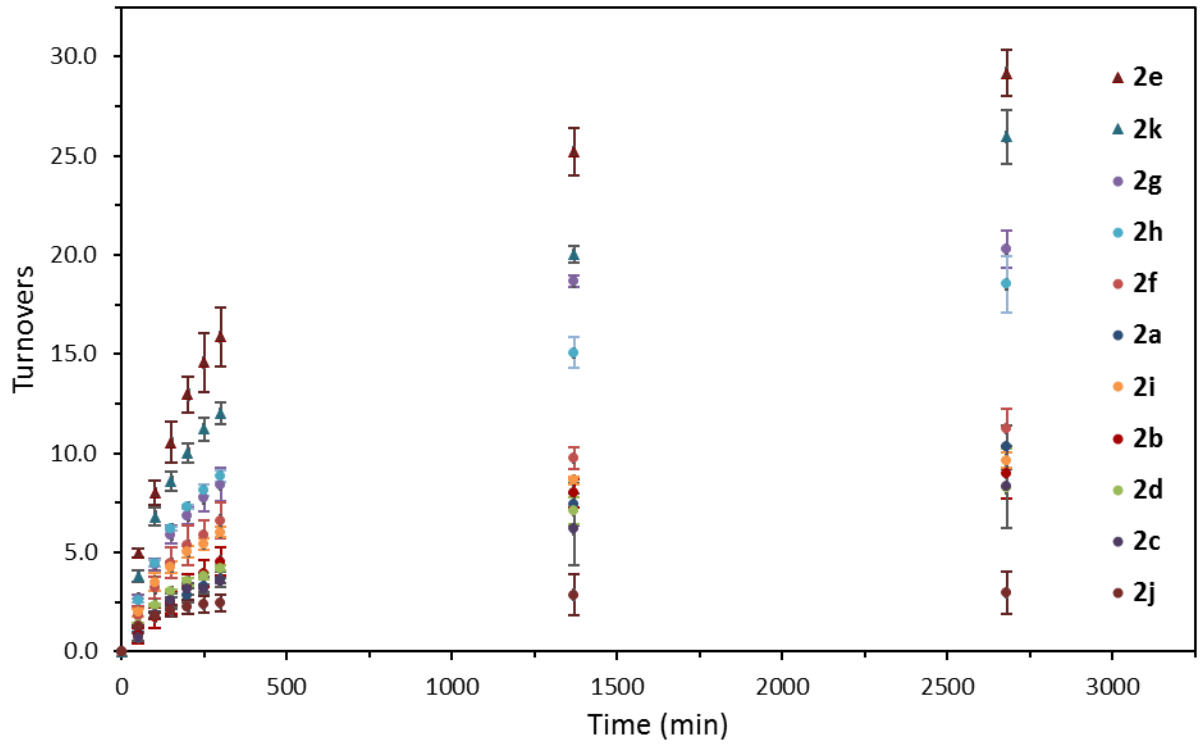



**Figure S3**. Monitored hydroarylation of ethylene (1 atm) with benzene-$d_6$ at 100 °C over 46 h by $^1$H NMR spectroscopy using catalysts **2a-k** (3.7 mM). Turnovers are given as the average of triplicate experiments with error calculated as the standard deviation.

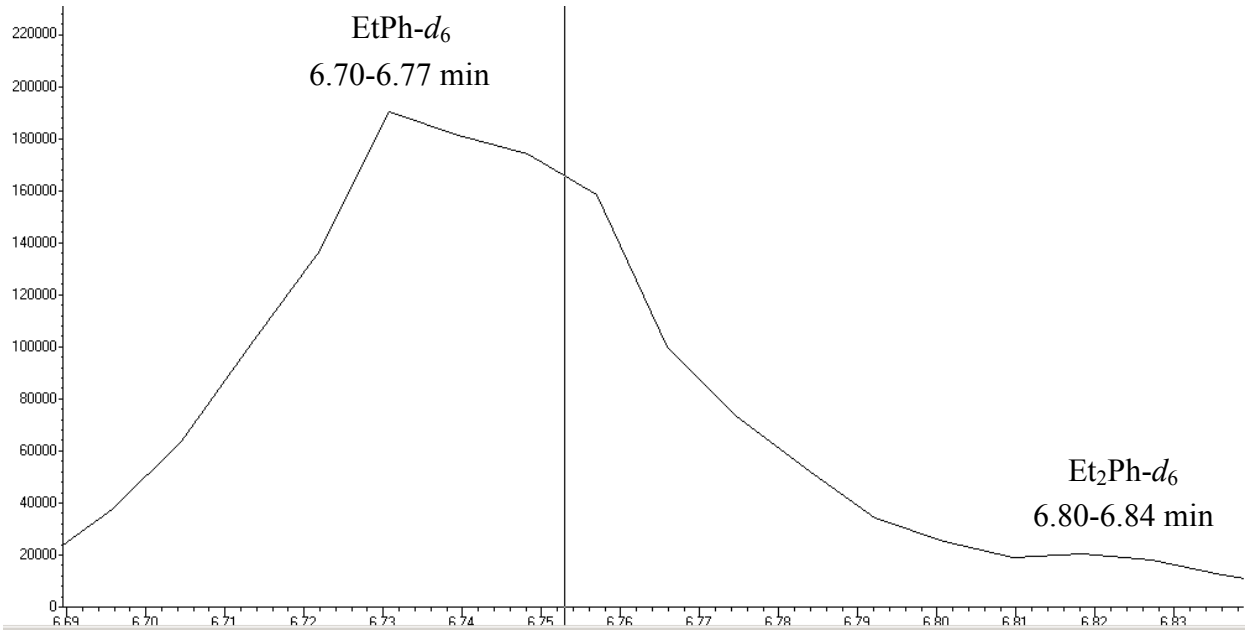



**Figure S4.** Representative chromatogram of catalytic ethylene hydroarylation with benzene-$d_6$ using catalysts **2a-k**. Ethylbenzene-$d_6$ (6.70-6.79 min) and diethylbenzenes-$d_6$ (6.78-6.84 min) are partially overlapping. Note that the sample was diluted in benzene as a carrier solvent in the GC-MS experiement. Additionally, note that the *ortho-, meta-, para*-isomers of diethylbenzene could not be resolved.

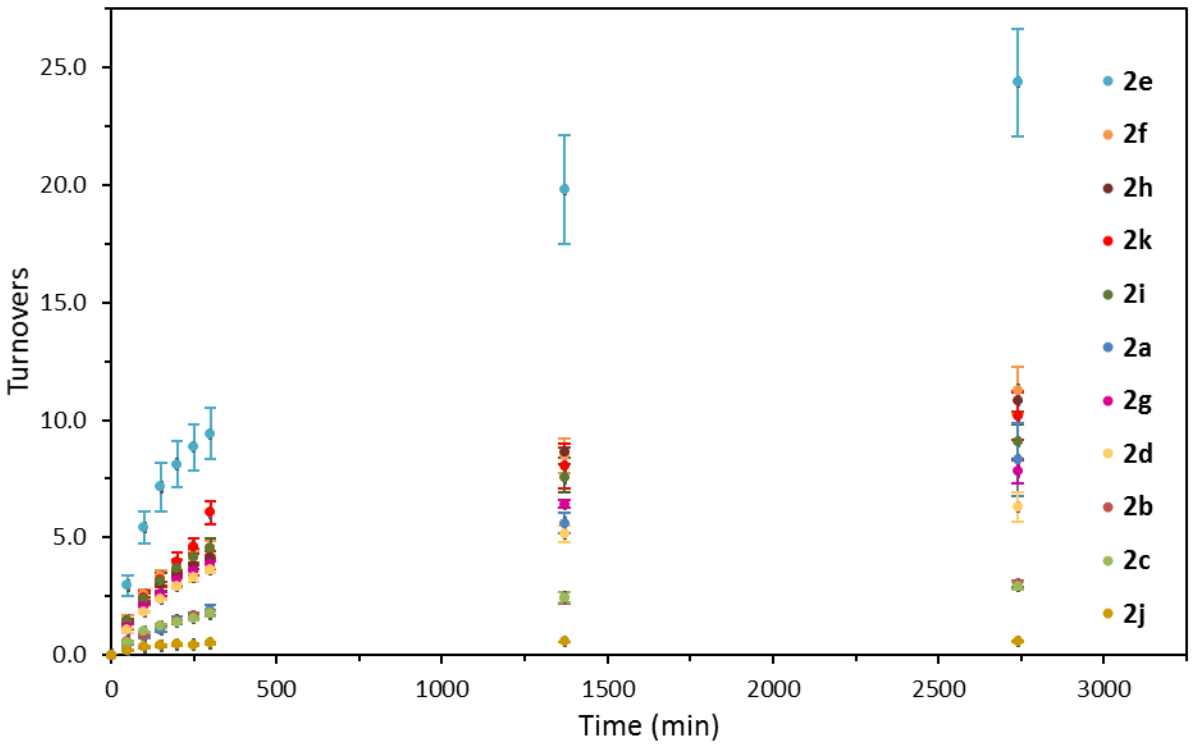



**Figure S5.** Monitored hydroarylation of propylene (1 atm) with benzene-$d_6$ at 100 °C over 46 h by $^1$H NMR spectroscopy using catalysts **2a-k** (3.7 mM). Turnovers are given as the average of triplicate experiments with error calculated as the standard deviation.

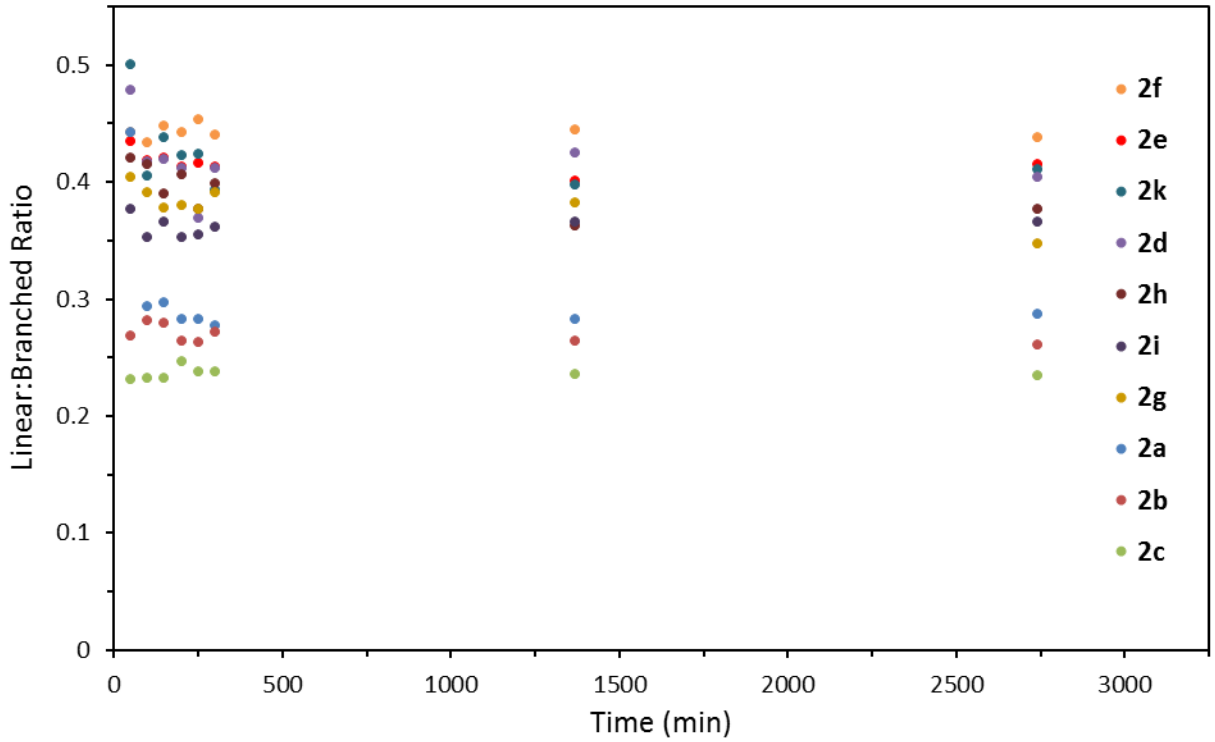



**Figure S6.** Monitored product regioselectivity during hydroarylation of propylene (1 atm) with benzene-$d_6$ at 100 °C over 46 h by $^1$H NMR spectroscopy using catalysts **2a-k** (3.7 mM) [note: catalyst **2j** is omitted; error bars have been omitted for clarity]. Selectivities determined as the ratio of $TO_{Linear}$:$TO_{Branched}$ and values are given as the average of triplicate experiments.

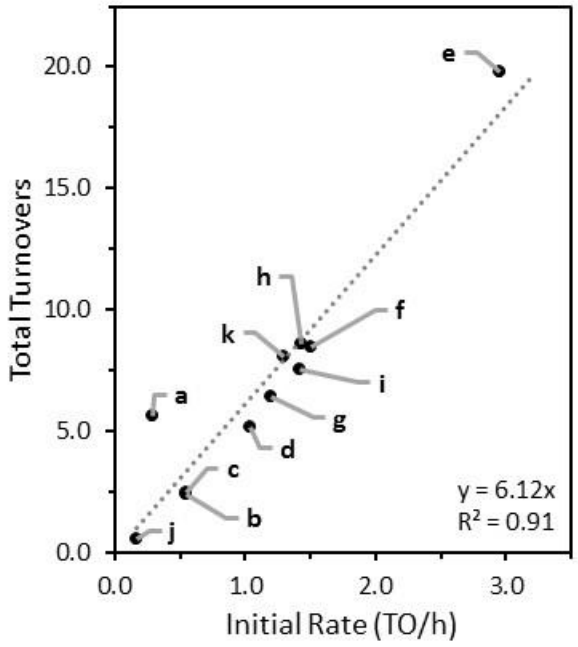



**Figure S7.** Plot of total turnovers from the hydroarylation of propylene with benzene-$d_6$ using catalysts **2a**-**2k** (measured at 24 h) vs. the initial product formation rate (measured as the turnovers after 1 h). Turnovers represent the sum of turnovers for cumene-$d_6$ and *n*-propylbenzene-$d_6$. The dashed line is a linear fit of the data.

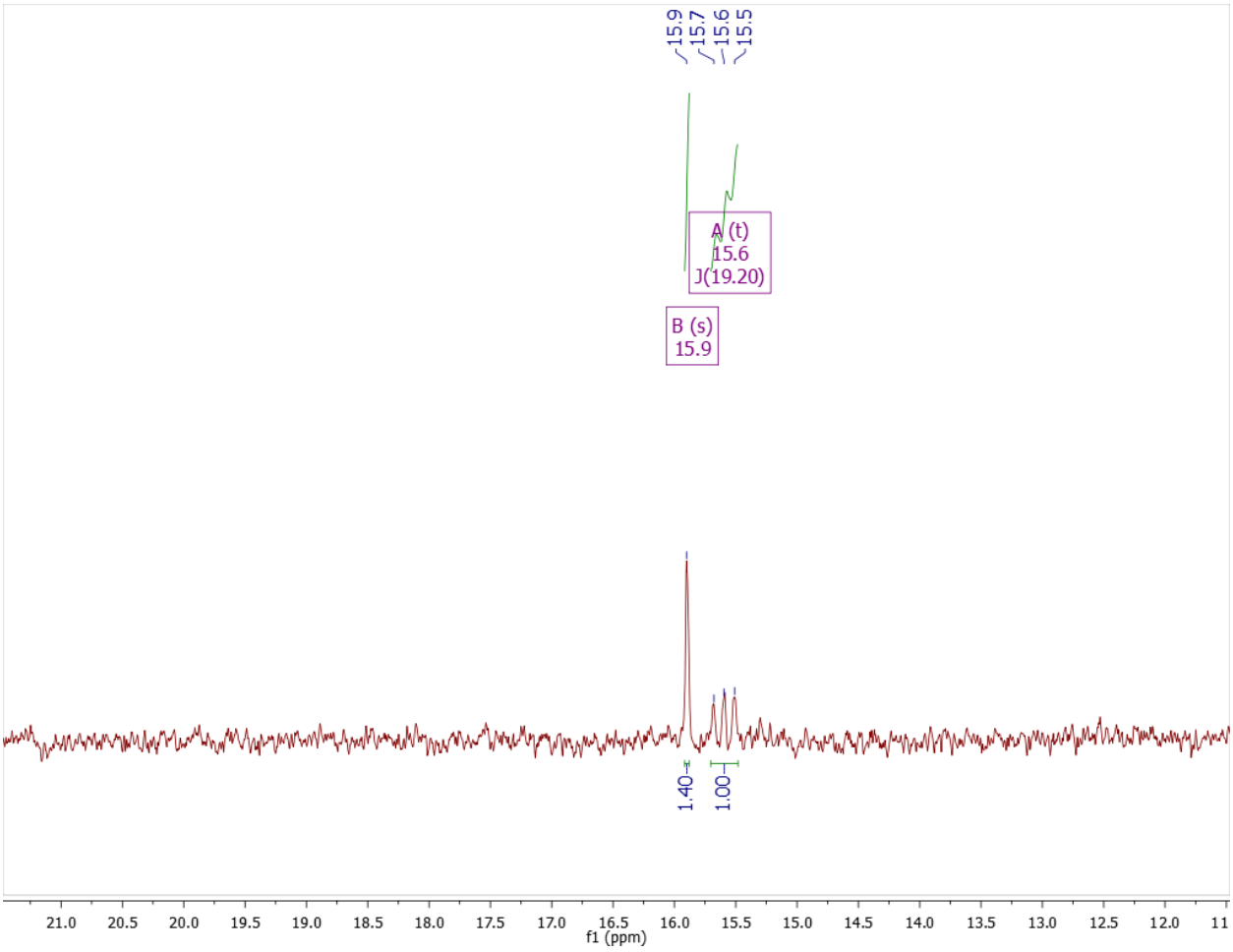



**Figure S8.** $^{13}C\{^{1}H\}$ NMR spectrum of the resulting products [$C_6H_5(CH_2CH_3)$ at 15.9 ppm and $C_6D_5(CH_2CH_2D)$ at 15.6 ppm] from competitive hydroarylation of ethylene with **2a** in an equimolar mixture of benzene and benzene-$d_6$. Note that methyl resonances in ethylbenzene-$d_6$ appear as a t due to C–D coupling ($J_{^2H^{13}C}$ = 19.2 Hz).

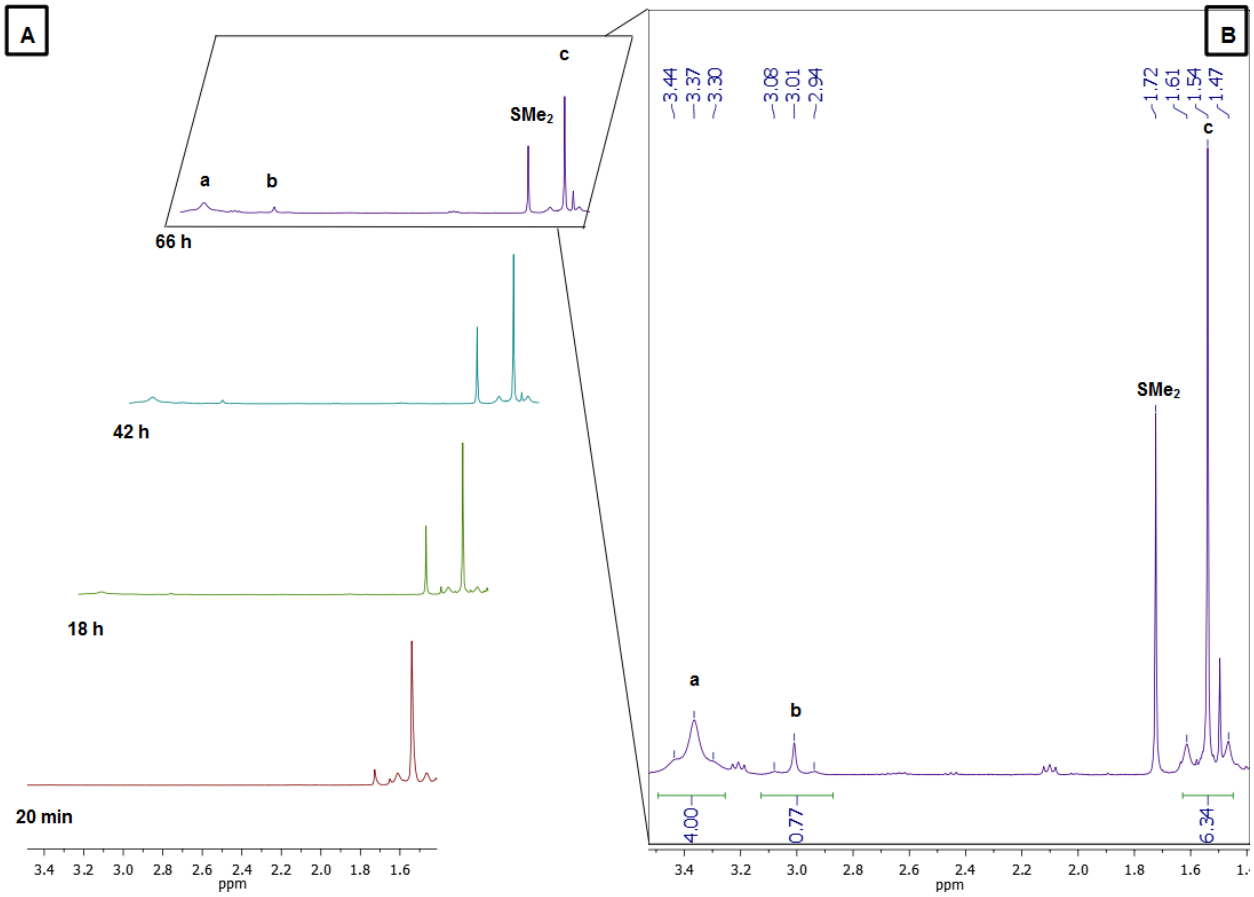



**Figure S9.** $^{1}$H NMR spectra of Pt speciation during ligand substitution reaction after exposure of **2a** to ethylene (1 atm) at ambient temperature. Resonance **a** (3.37 ppm, $J_{PtH}$ = 59 Hz) is the $C_2H_4$ fragment of complex **3**. Resonance **b** (3.01 ppm, $J_{PtH}$ = 54 Hz) is the $C_2H_4$ fragment of complex **4**. Resonance **c** (1.54 ppm, $J_{PtH}$ = 53 Hz) is the $SMe_2$ fragment of complex **2a**. Free $SMe_2$ is observed at 1.72 ppm. **Insert A**: Monitored $^{1}$H NMR spectra of the substitution reaction over the course of 3 days. Note that resonances **a**, **b**, and **$SMe_2$** grow in intensity over time while resonance **c** decays. **Insert B**: Expansion of the $^{1}$H NMR spectra after 66 h of exposure to $C_2H_4$. Note the relative ratio of the integrations of resonances **c**, **a**, and **b** are ca. 6.3:4.0:0.8, respectively. This corresponds to the observed product ratio of **2a**:**3**:**4** of 1.1:1.0:0.2, respectively.

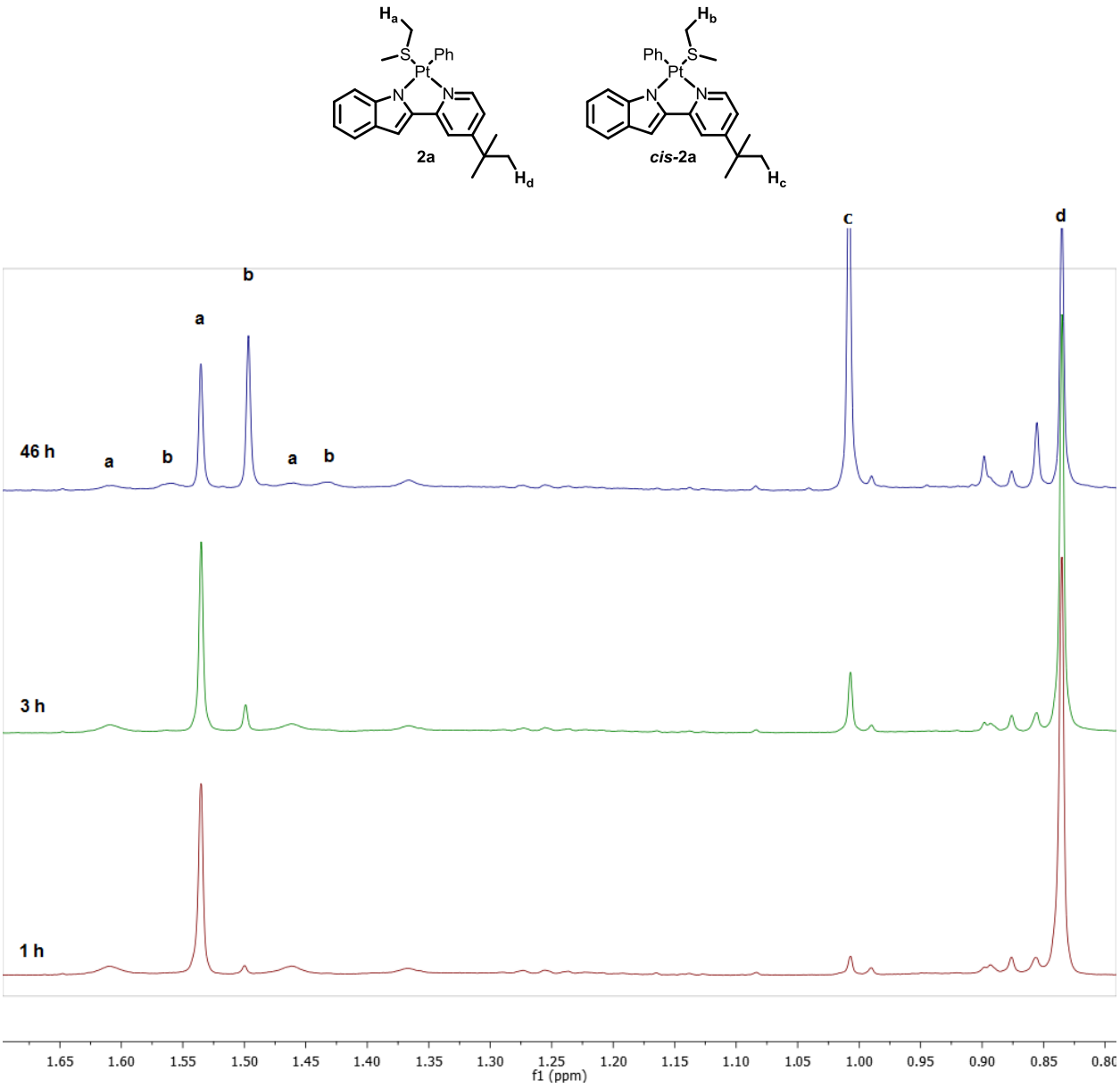



**Figure S10.** Monitored thermolysis of complex **2a** at 100 °C in benzene-$d_6$. Lower: $^1$H NMR spectrum after 1 h of heating. Middle: $^1$H NMR spectrum after 3 h of heating. Upper: $^1$H NMR spectrum after 46 h of heating. Selected resonances shown above for compound **2a**: δ 1.54 (s, $J_{PtH}$ = 60 Hz, **a**), 0.84 (s, **d**). Selected resonances above for compound ***cis*-2a**: δ 1.50 (s, $J_{PtH}$ = 52 Hz, **b**), 1.01 (s, **c**). Aryl protons for **2a** and *cis*-**2a** overlap, making individual peak assignment difficult.

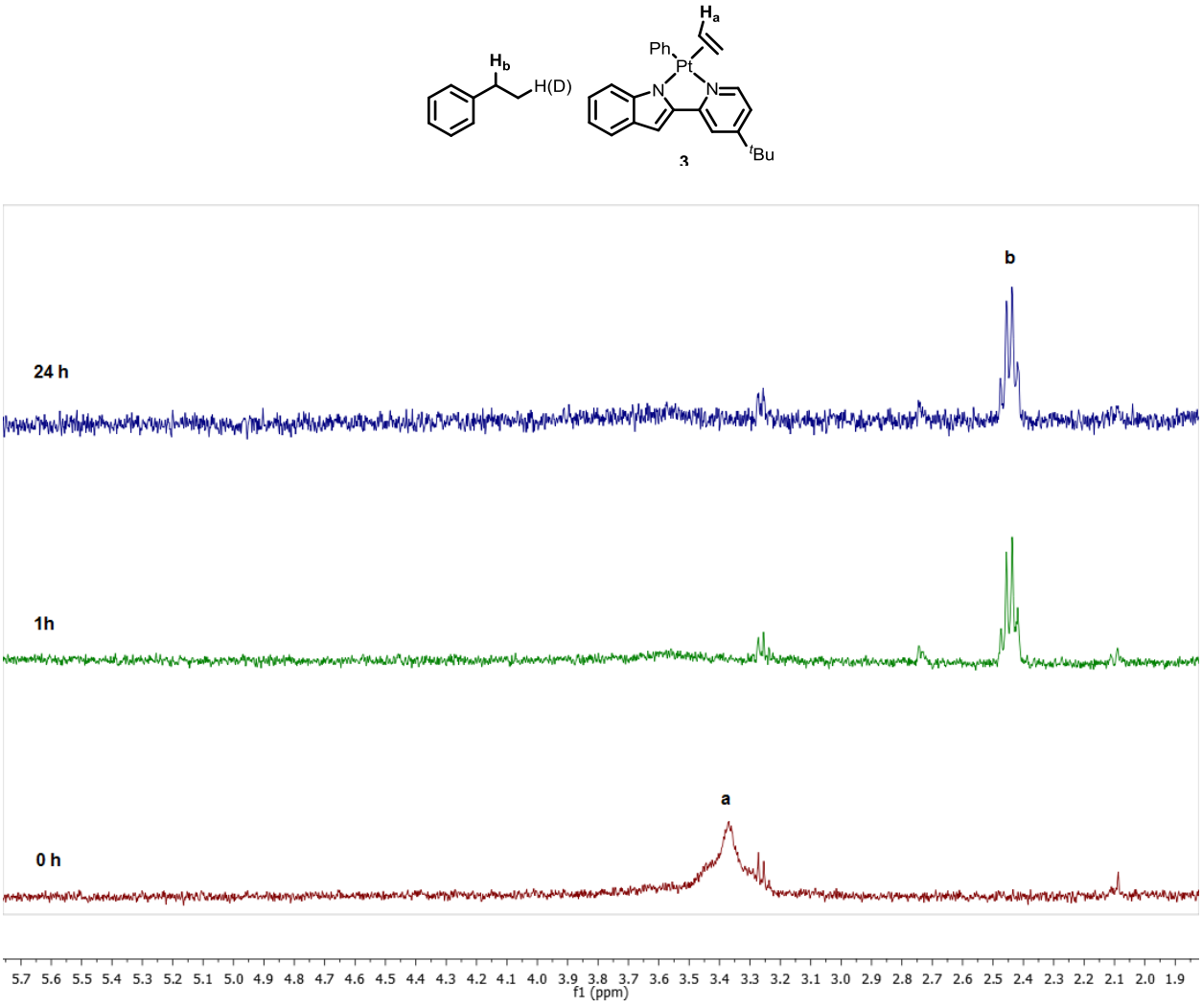
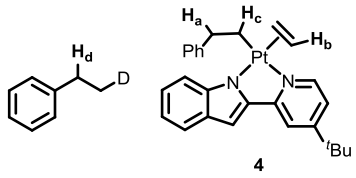



**Figure S11.** Monitored thermolysis of complex **3** at 100 °C in benzene-$d_6$. Lower: initial $^1$H NMR spectrum prior to heating. Middle: $^1$H NMR spectrum after 1 h of heating. Upper: $^1$H NMR spectrum after 24 h of heating. Selected resonances shown above for compound **3**: 3.83 (s, $J_{PtH}$ = 59 Hz, **a**). Rapid decomposition of **3** occurs with concurrent ethylbenzene formation. Note that H(D) exchange appears to occur to produce a mixture of ethylbenzene-$d_1$ and ethylbenzene-$d_0$.



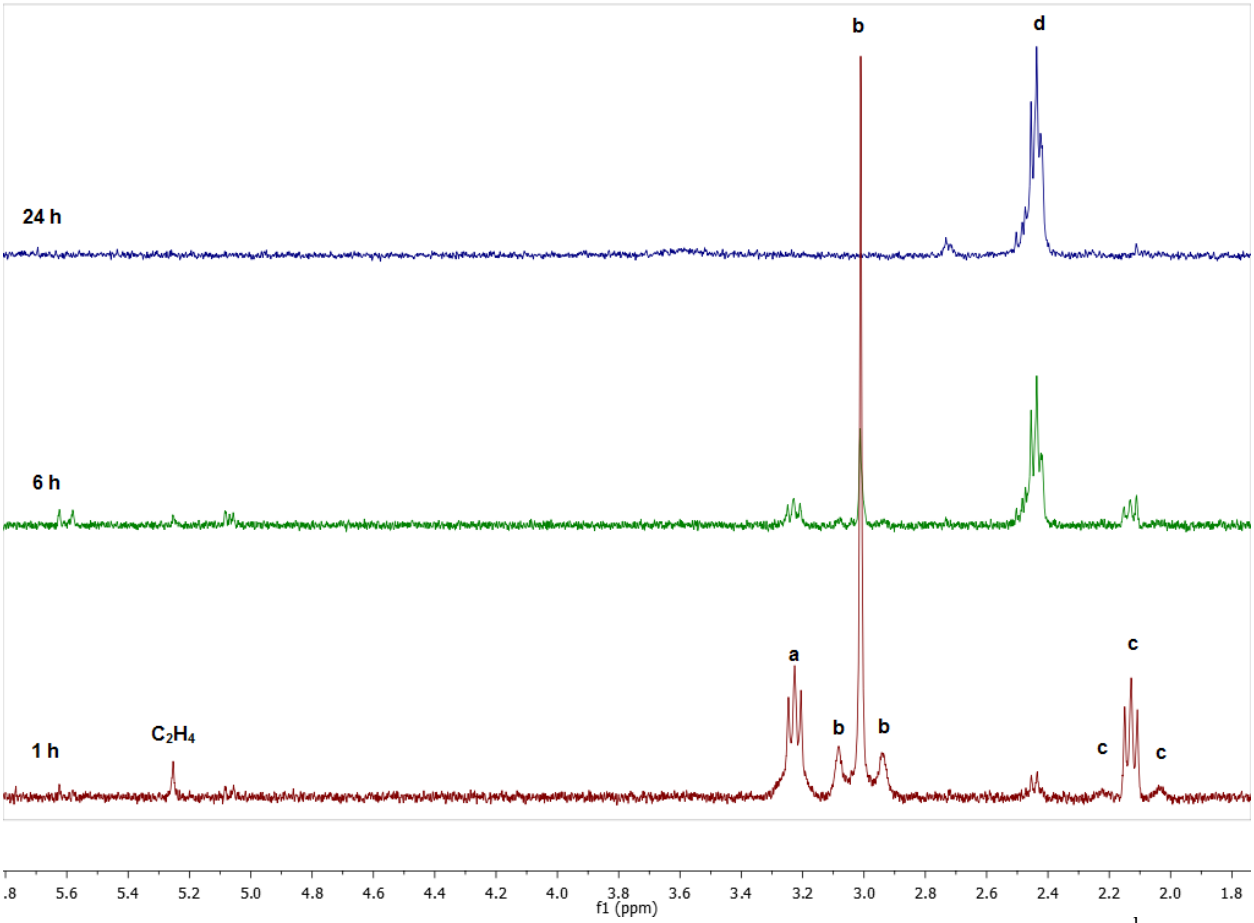




**Figure S12.** Monitored thermolysis of complex **4** at 100 °C in benzene-$d_6$. Lower: $^1$H NMR spectrum after 1 h of heating. Middle: $^1$H NMR spectrum after 3 h of heating. Upper: $^1$H NMR spectrum after 24 h of heating. Selected resonances shown above for compound **4**: δ 3.22 (t, $J$ = 8.1 Hz, **a**), 3.01 (s, $J_{PtH}$ = 54 Hz, **b**), 2.12 (t, $J_{HH}$ = 8.2 Hz, $J_{PtH}$ = 67 Hz, **c**). Ethylene resonance at 5.25 noted during early time points of heating. Ethylbenzene benzylic resonance (**d**) noted after 1 h and rapidly increased as **4** decomposed.

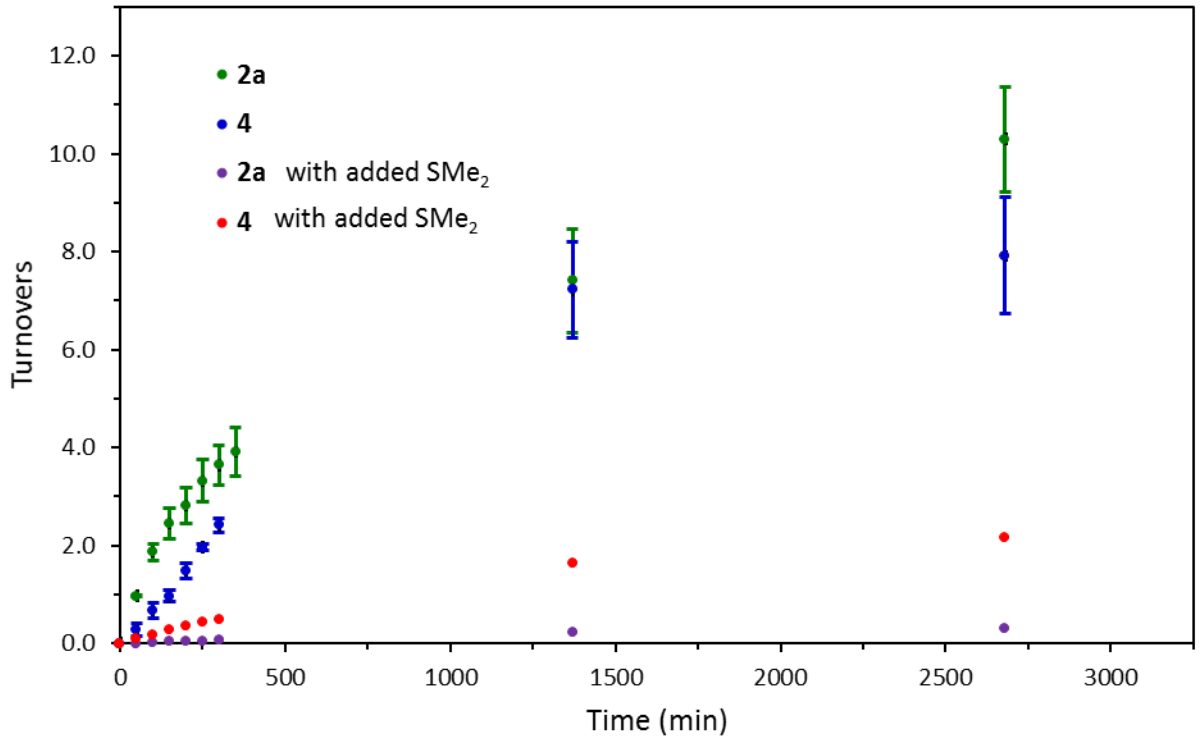



**Figure S13.** Monitored hydroarylation of ethylene (1 atm) with benzene-$d_6$ at 100 °C over 144 h by $^1$H NMR spectroscopy using catalysts **2a** and **4** (3.7 mM) with and without added $SMe_2$ in the reaction mixture. Turnovers are given as the average of triplicate experiments with error calculated as the standard deviation.

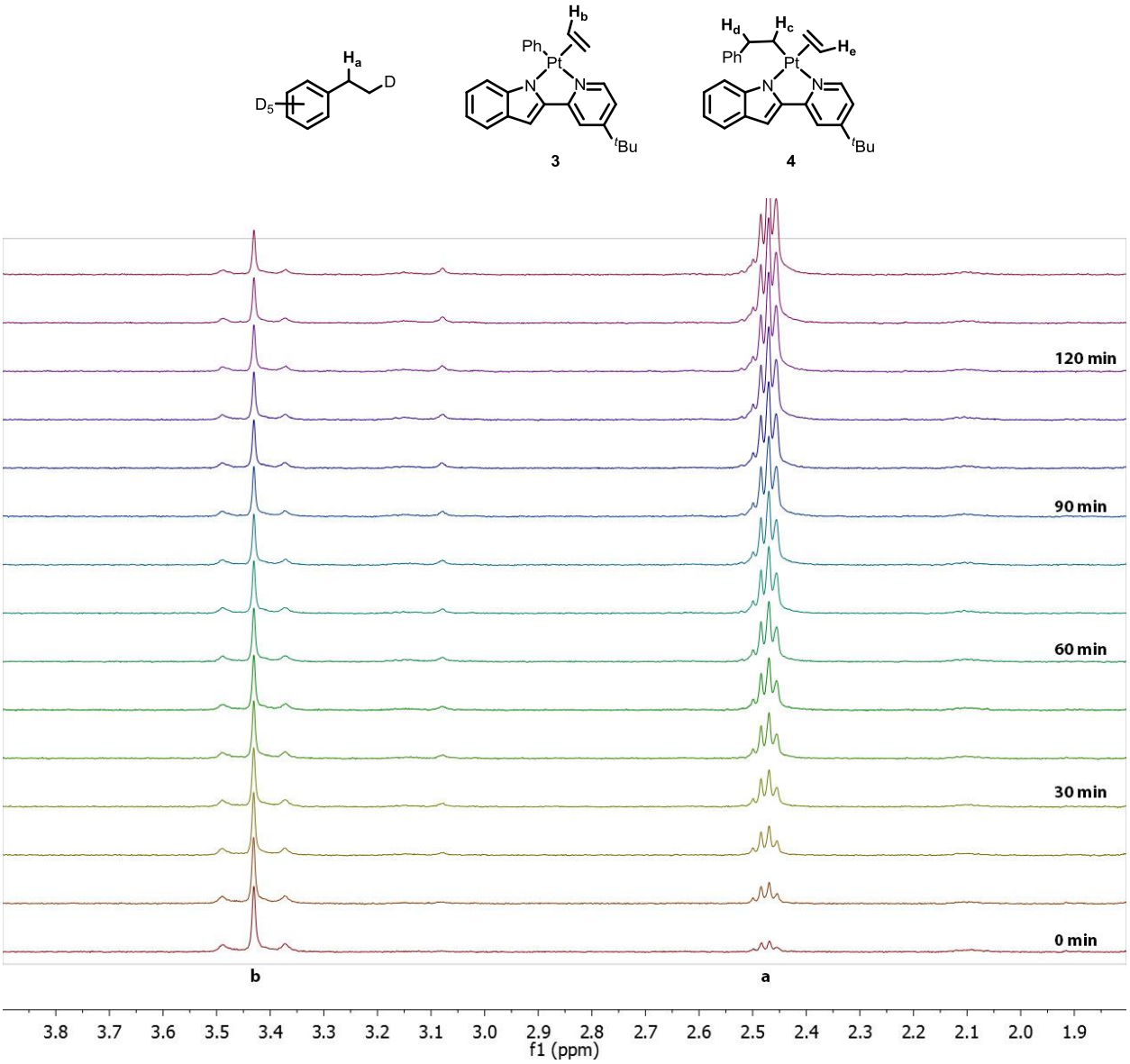



**Figure S14.** Variable temperature $^{1}$H NMR of **2a** at 80 °C in benzene-$d_6$. Scans were taken once every 10 min during the course of the reaction (over a 2 h period). The resonance corresponding to bound ethylene in **3** (**b**) was observed at the first scan after being heated in the NMR spectrometer. Additionally, free $SMe_2$ was noted as well as bound $SMe_2$ (not shown). Full conversion of **2a** to **3**, therefore, was not observed. Conversion of ethylene and benzene-$d_6$ to ethylbenzene-$d_6$ was rapidly observed, as noted by the formation of the ethlbenzene-$d_6$ benzylic peak (**a**). Complex **4** was not observed to a major extent during the course of the variable temperature $^{1}$H NMR experiment.

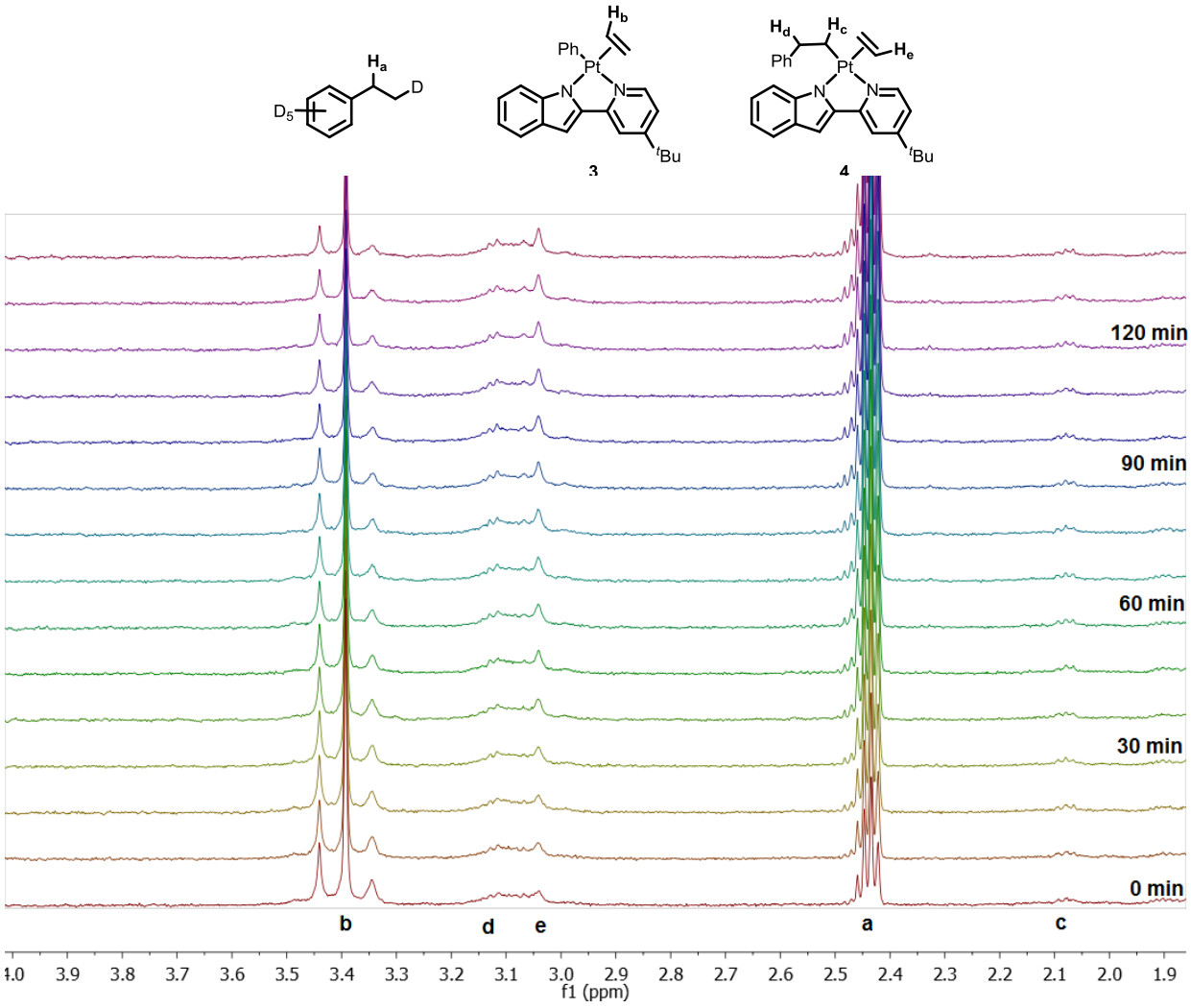



**Figure S15.** Variable temperature $^{1}$H NMR of **3** at 80 °C in benzene-$d_6$. Scans were taken once every 10 min during the course of the reaction (over a 2 h period). Bound ethylene resonances (**b**) for complex **3** were noted in every time point of the experiment, and only slowly reduced in intensity over time. Resonances corresponding to complex **4** (**c**, **d,** and **e**) only slowly grew in intensity during the reaction. Rapid formation of ethylbenzene-$d_6$ (**a**) was noted during the course of the reaction.

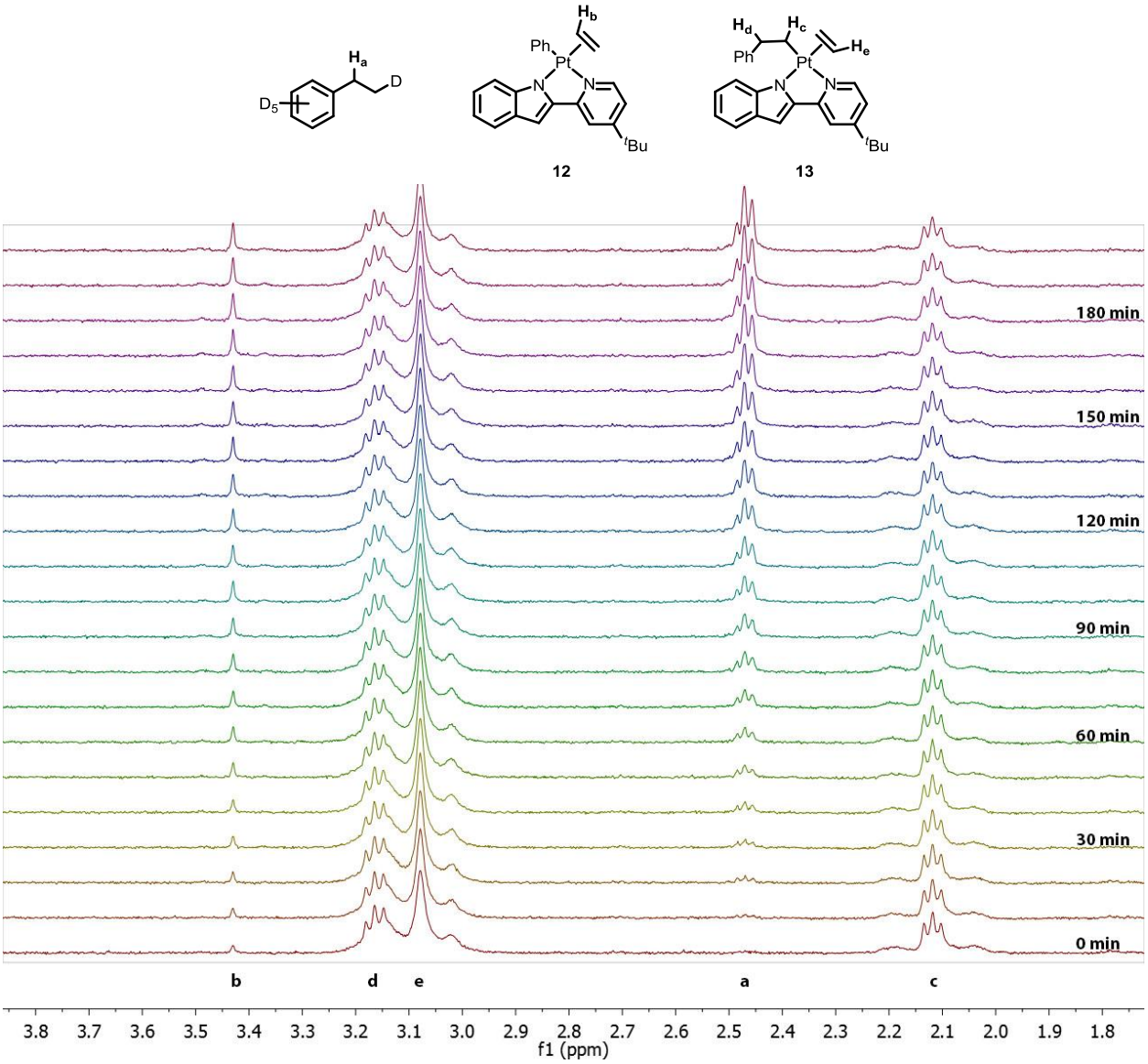



**Figure S16.** Variable temperature $^{1}$H NMR of **4** at 80 °C in benzene-$d_6$. Scans were taken once every 10 min during the course of the reaction (over a 3 h period). Bound ethylene resonances (**b**) for complex **3** only slowly grew in intensity during the reaction. Resonances corresponding to complex **4** (**c**, **d,** and **e**) were present during the entirety of the experiment, and only decreased in intensity slowly during the reaction. Slow formation of ethylbenzene-$d_6$ (**a**) was noted during the course of the reaction.

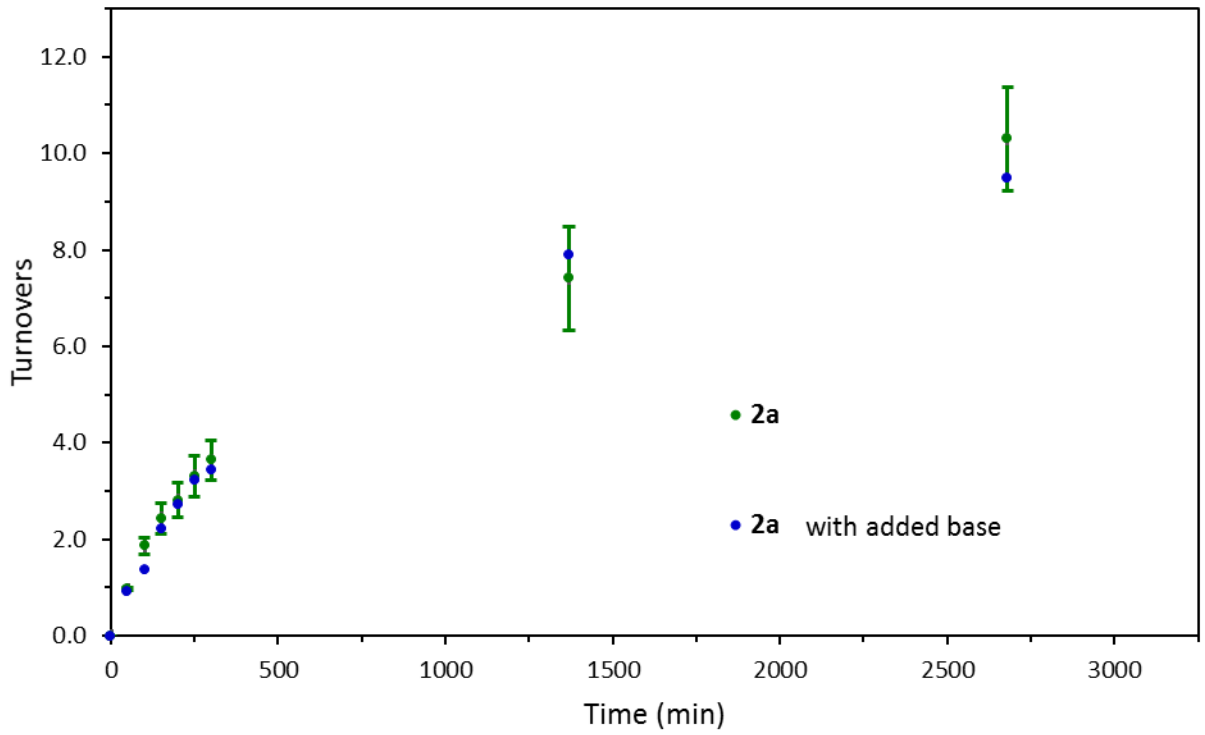



**Figure S17.** Monitored hydroarylation of ethylene (1 atm) with benzene-$d_6$ at 100 °C over 46 h by $^1$H NMR spectroscopy using catalyst **2a** (3.7 mM) with (blue) and without added 2,6-di-*tert*-butyl-4-methylpyridine (green). Turnovers are given as the average of triplicate experiments with error calculated as the standard deviation.

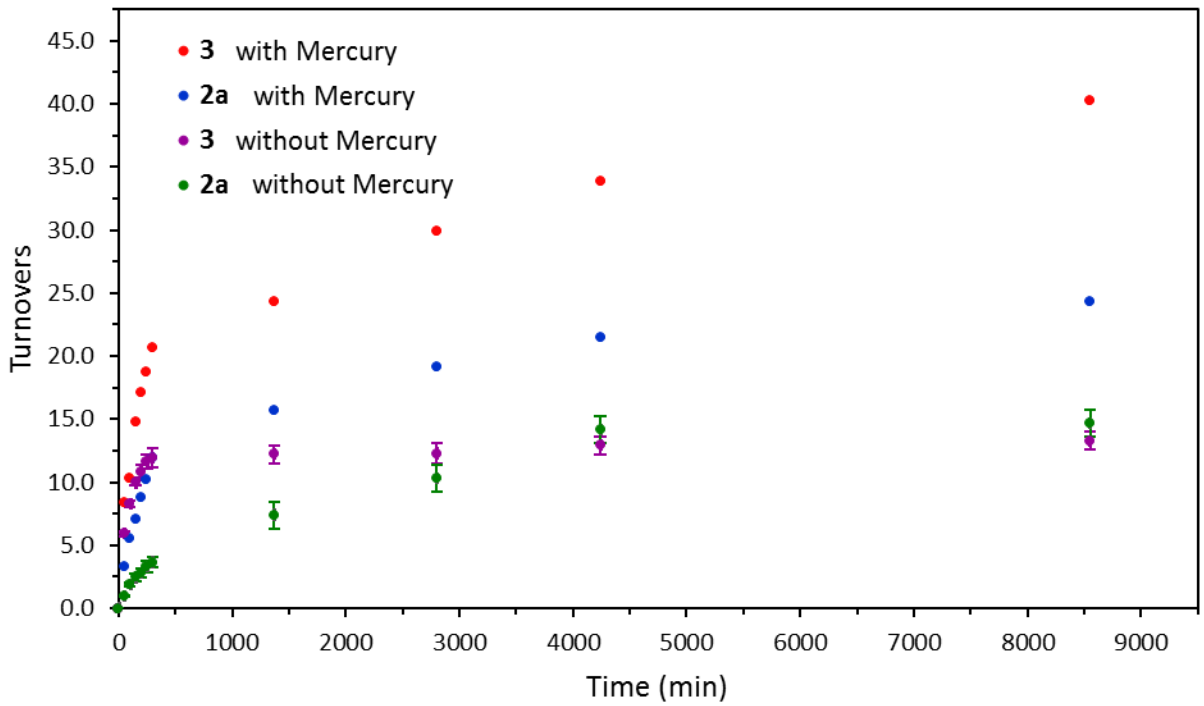



**Figure S18.** Monitored hydroarylation of ethylene (1 atm) with benzene-$d_6$ at 100 °C over 144 h by $^1$H NMR spectroscopy using catalysts **2a** and **3** (3.7 mM) with and without the presence of Hg(0) in the reaction mixture. Turnovers are given as the average of triplicate experiments with error calculated as the standard deviation.

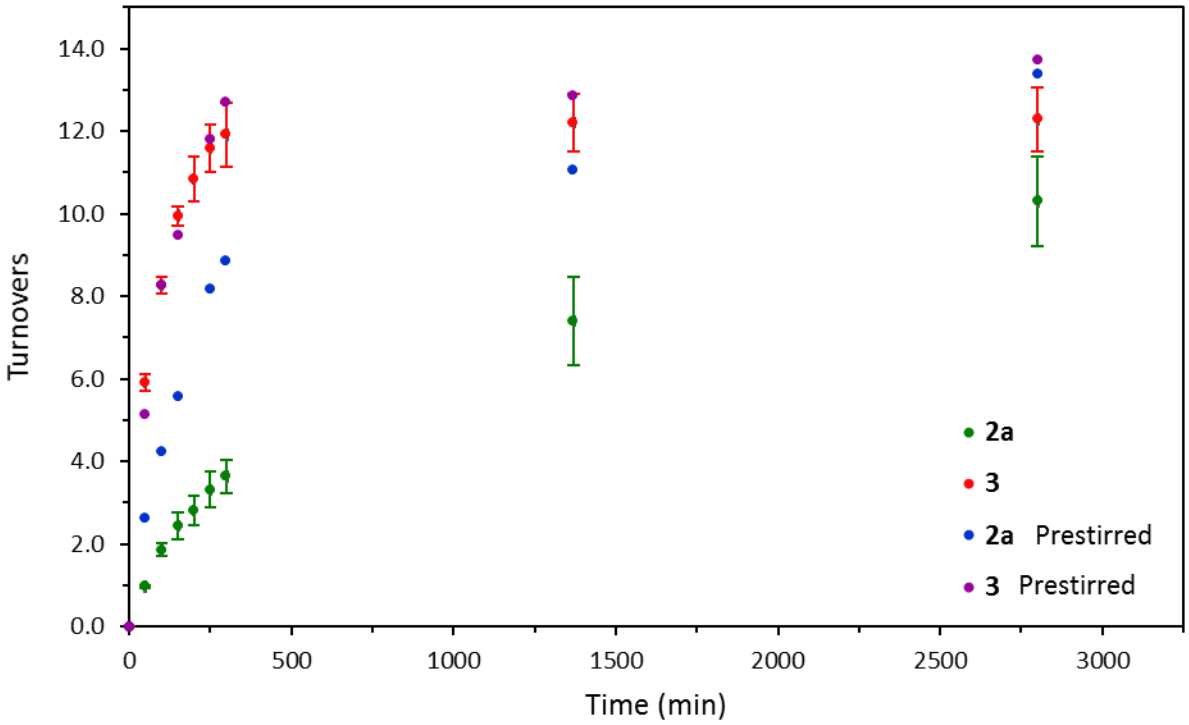



**Figure S19.** Monitored hydroarylation of ethylene (1 atm) with benzene-$d_6$ at 100 °C over 46 h by $^1$H NMR spectroscopy using catalysts **2a** and **3** (3.7 mM) with and without prestirring the catalysts with Hg(0) prior to olefin addition. Mercury was removed prior to substrate addition and heating. Turnovers are given as the average of triplicate experiments with error calculated as the standard deviation.

## TABLES

**Table S1.** Decomposition products identified by HRMS (ESI-TOF) after ethylene hydroarylation with catalyst **2a** in benzene at 100 °C for 20 h. Masses of proposed structures (as the $H^+$ or $K^+$ species) are given under the Theoretical *m*/*z*.

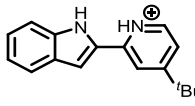
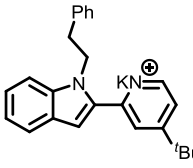
| Found *m*/*z* | Theoretical *m*/*z* | Assignment (Compound Number) |
|---|---|---|
| 251.1559 | $[M + H]^+$ Calcd for $C_{17}H_{19}N_2$, 251.154. |  (**1a**) |
| 393.2098 | $[M + K]^+$ Calcd for $C_{25}H_{26}N_2K$, 393.1728. |  (**5**) |
| 536.1706 | $[M + H]^+$ Calcd for $C_{21}H_{29}N_2PtS$, 536.1694 | $[(^t\text{BuPyInd})PtEt(SMe_2)]H^+$ (**7**) |
| 550.1831 | $[M + H]^+$ Calcd for $C_{25}H_{27}N_2Pt$, 550.1816. | $[(^t\text{BuPyInd})PtPh(C_2H_4)]H^+$ (**3**) |
| 584.1706 | $[M + H]^+$ Calcd for $C_{25}H_{29}N_2PtS$, 584.1694. | $[(^t\text{BuPyInd})PtPh(SMe_2)]H^+$ (**2a**) |
| 612.2007 | $[M + H]^+$ Calcd for $C_{27}H_{33}N_2PtS$, 612.2007. | $[(^t\text{BuPyInd})Pt(CH_2CH_2Ph)(SMe_2)]H^+$ (**6**) |
| 626.1817 | $[M + H]^+$ Calcd for $C_{31}H_{31}N_2Pt$, 626.2129. | $[(^t\text{BuPyInd})PtPh(H_2C{=}CHPh)]H^+$ (**8**) |

**Table S2.** Summary of Crystallographic Data for Complexes **2a-c**, **3**, and **4**.

| Compound | **2a** | **2b** | **2c** | **3** | **4** |
|---|---|---|---|---|---|
| Empirical Formula | $C_{25}H_{28}N_2PtS$ | $C_{25}H_{26}F_2N_2PtS$ | $C_{25}H_{24}F_4N_2PtS$ | $C_{25}H_{26}N_2Pt$ | $C_{27}H_{30}N_2Pt$ |
| Formula Mass | 583.64 | 619.64 | 655.62 | 549.58 | 577.62 |
| Crystal System | Monoclinic | Triclinic | Triclinic | Monoclinic | Monoclinic |
| Space Group | C2/c | P-1 | P-1 | C2/c | $P2_1/c$ |
| a (Å) | 25.6857(8) | 9.0052(4) | 8.9213(5) | 30.2380(10) | 9.0700(3) |
| b (Å) | 11.6427(4) | 10.3193(5) | 10.1362(5) | 12.4961(4) | 22.5628(8) |
| c (Å) | 18.7609(6) | 13.9951(6) | 14.7554(8) | 13.1254(4) | 10.8200(4) |
| α (°) | 90 | 90.135(2) | 97.236(3) | 90 | 90 |
| β (°) | 116.0020(10) | 92.418(2) | 90.819(3) | 106.172(2) | 96.155(2) |
| γ (°) | 90 | 94.402(2) | 94.146(3) | 90 | 90 |
| Unit Cell Volume ($Å^3$) | 5042.6(3) | 1295.52(10) | 1319.84(12) | 4763.3(3) | 2201.49(13) |
| Z | 8 | 2 | 2 | 8 | 4 |
| Crystal Size ($mm^3$) | 0.07 x 0.05 x 0.01 | 0.10 x 0.05 x 0.01 | 0.11 x 0.10 x 0.03 | 0.06 x 0.04 x 0.01 | 0.09 x 0.04 x 0.01 |
| Reflections Collected | 35910 | 29536 | 35194 | 30377 | 34268 |
| Independent Reflections | 4634 | 4718 | 4860 | 4379 | 4007 |
| $R_{int}$ | 0.0267 | 0.0276 | 0.0266 | 0.0536 | 0.0398 |
| Completeness to θ = 25.000° (%) | 100.0 | 99.4 | 99.9 | 100.0 | 99.6 |
| Final *R* indices (I > 2σ(I)) | 0.0139 | 0.0172 | 0.0131 | 0.0264 | 0.0230 |
| Final *R* indices (all data) | 0.0147 | 0.0178 | 0.0142 | 0.0381 | 0.0298 |
| Goodness-of-Fit of $F^2$ | 1.041 | 1.050 | 1.047 | 1.066 | 1.090 |

Note: Complete crystallographic data can be found in the CIF files and is available free of charge via the Internet at http://pubs.acs.org.

**NMR SPECTRA OF COMPOUNDS**

**Figure S20.** $^{1}H$ NMR of **S3a** in $CD_2Cl_2$.

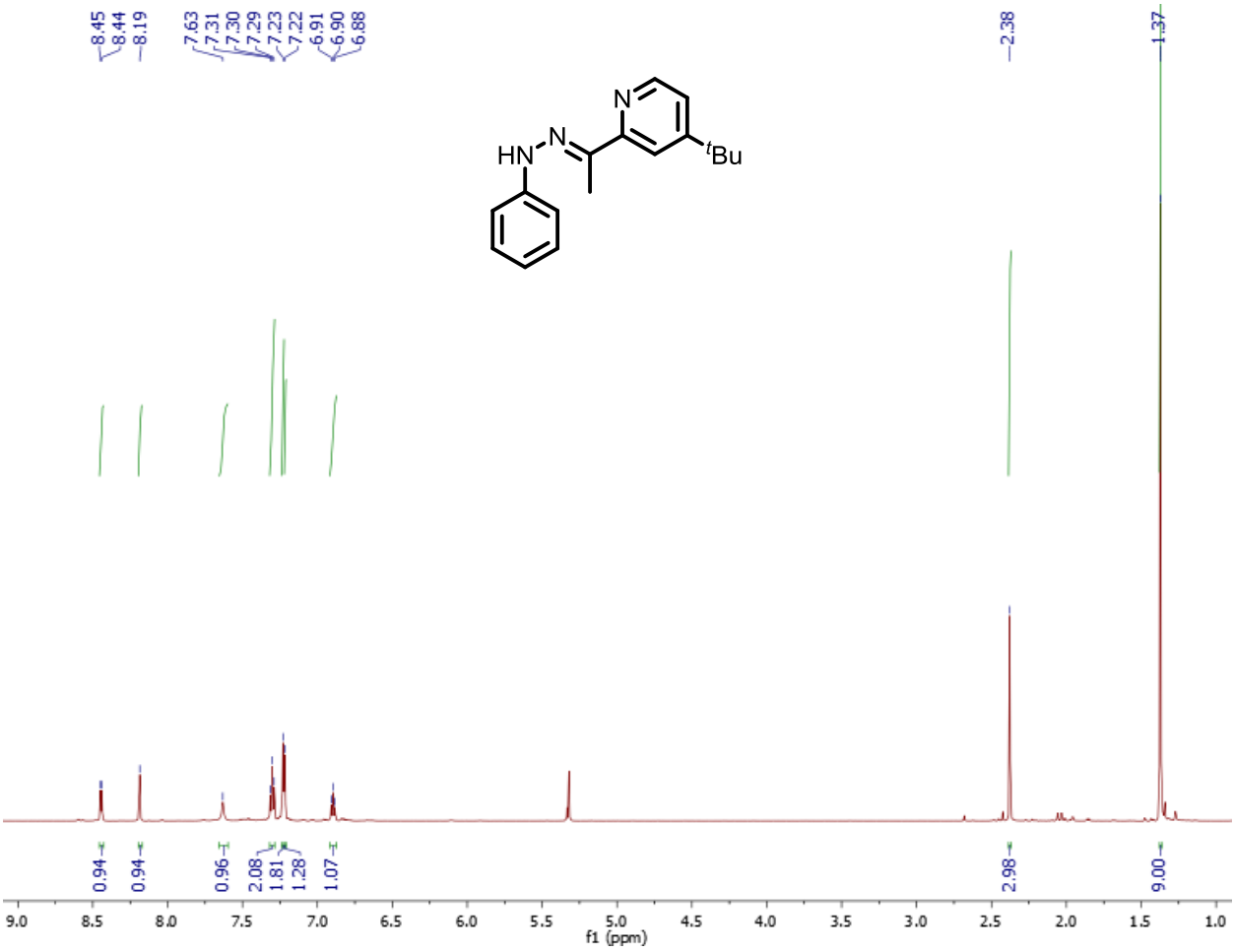


**Figure S21.** $^{13}C\{^{1}H\}$ NMR of **S3a** in $CD_2Cl_2$.

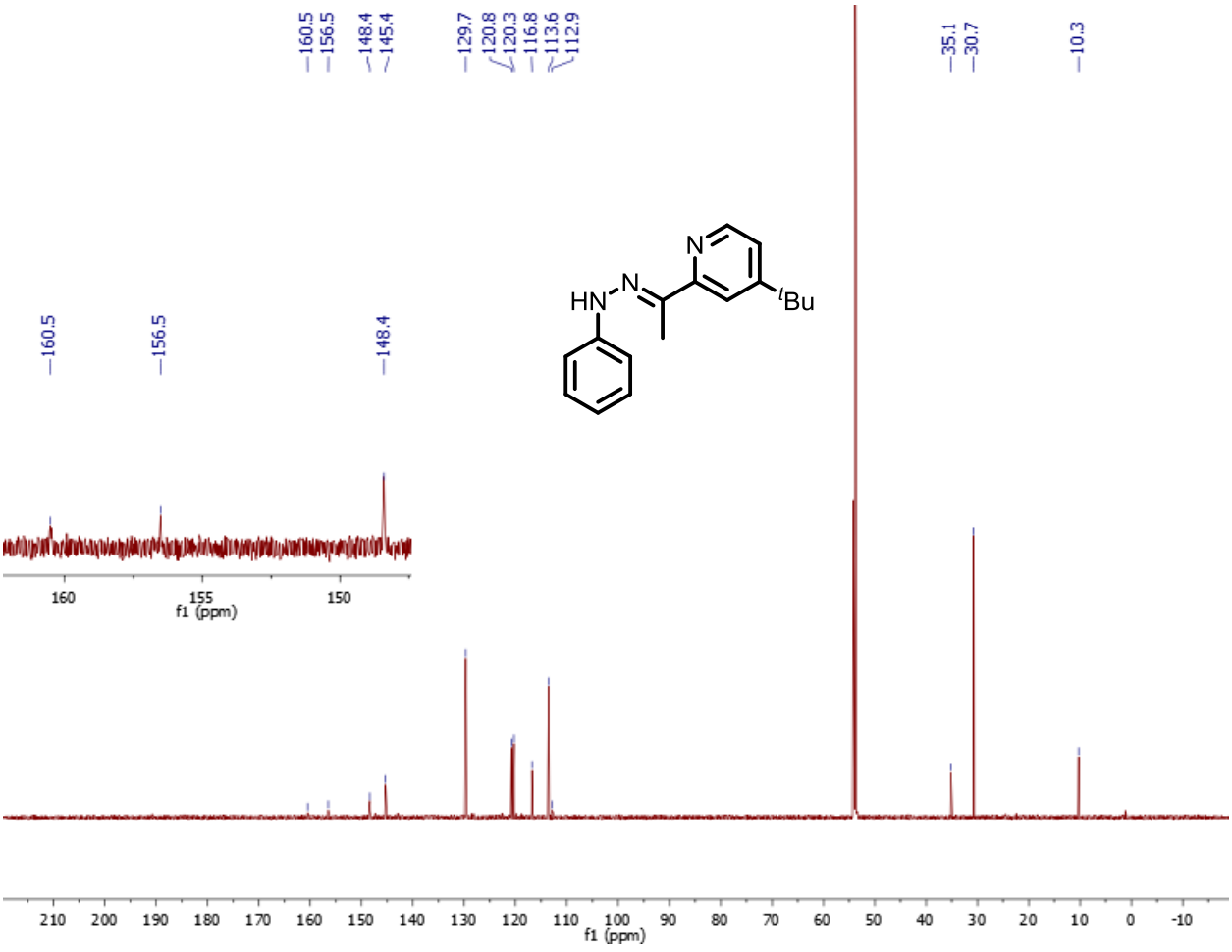


**Figure S22.** $^{1}H$ NMR of **1a** in $CD_2Cl_2$.

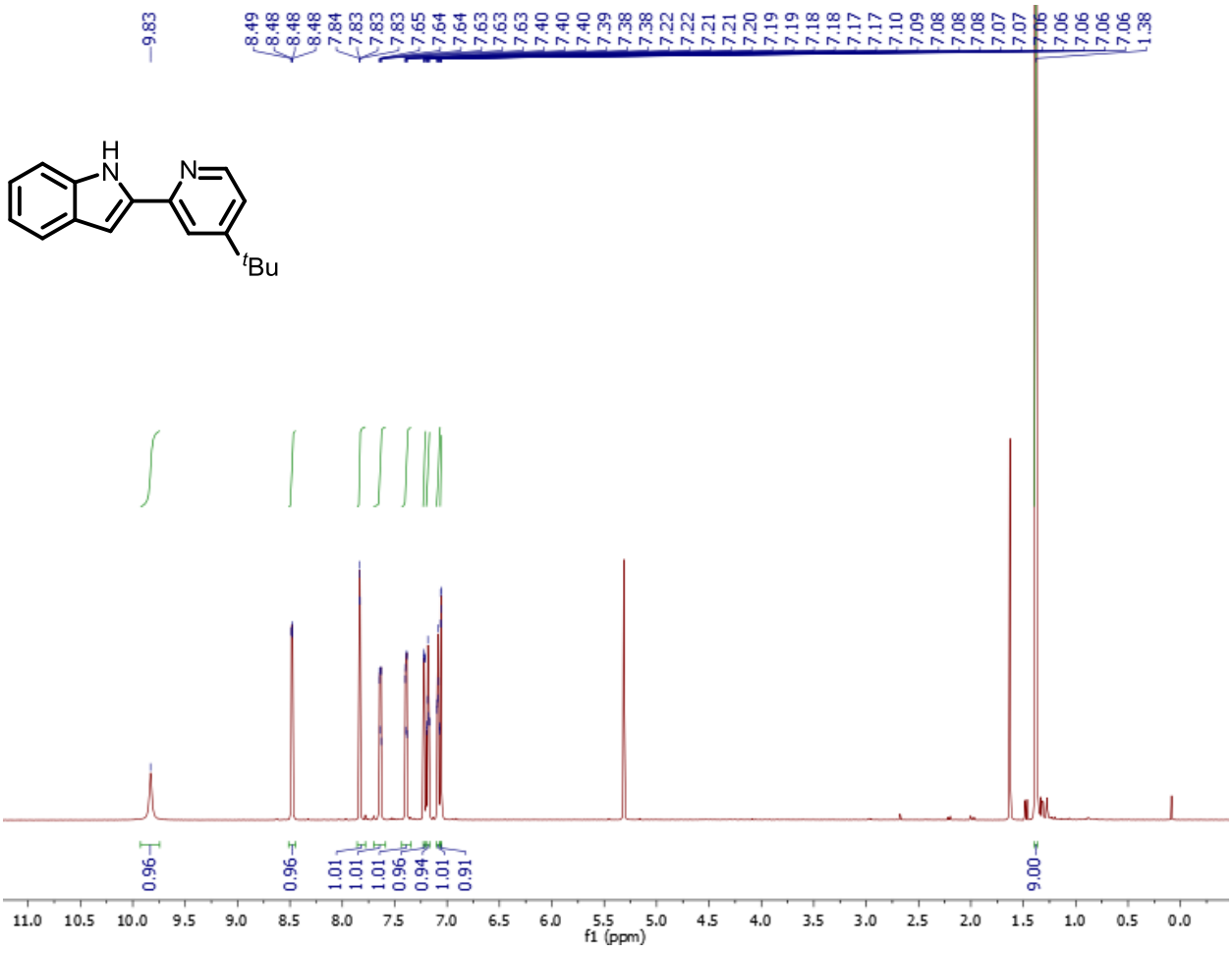


**Figure S23.** $^{13}C\{^{1}H\}$ NMR of **1a** in $CD_2Cl_2$.

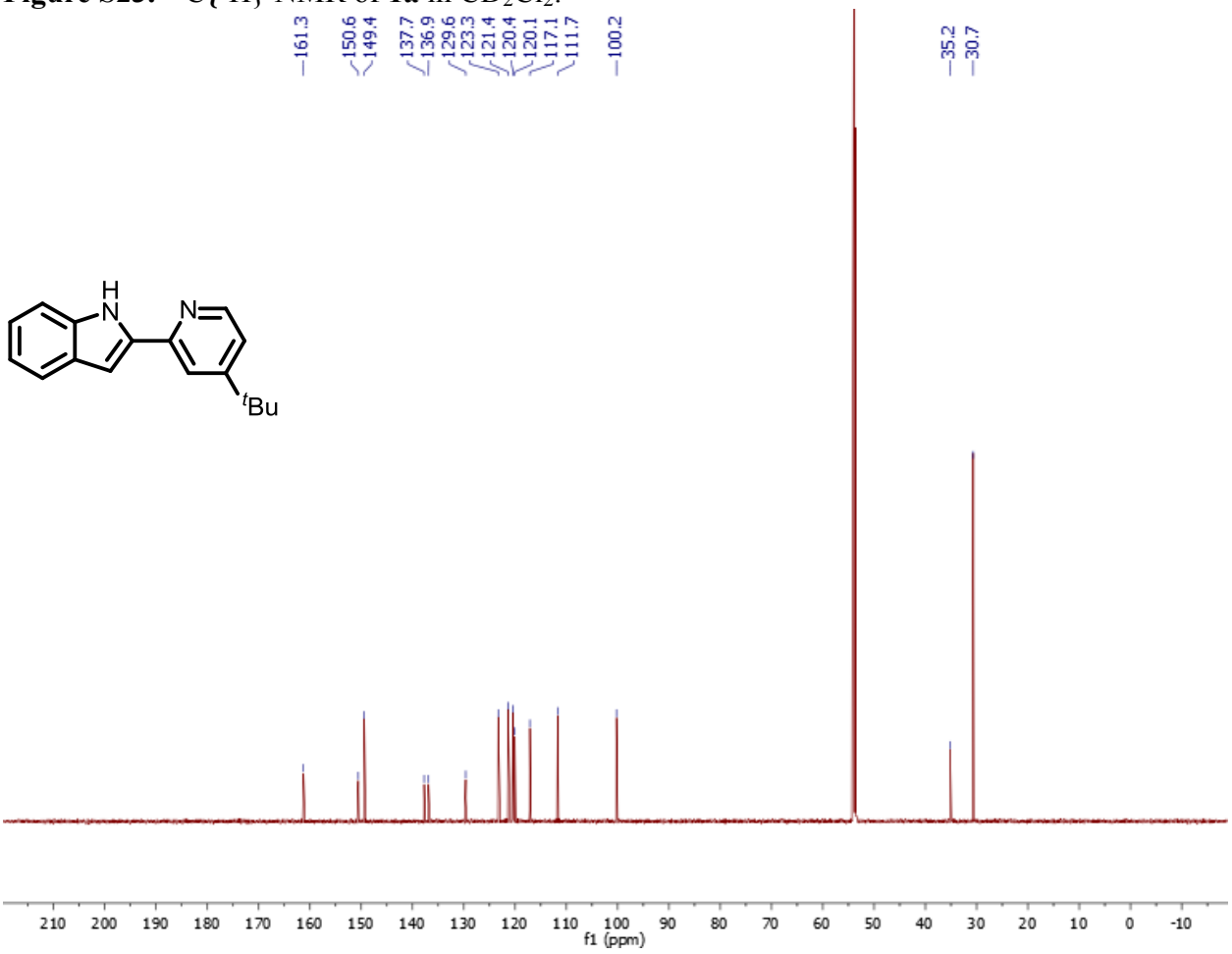


**Figure S24.** $^{1}$H NMR of **2a** in $C_6D_6$. Insert: enlargement of aryl resonances.

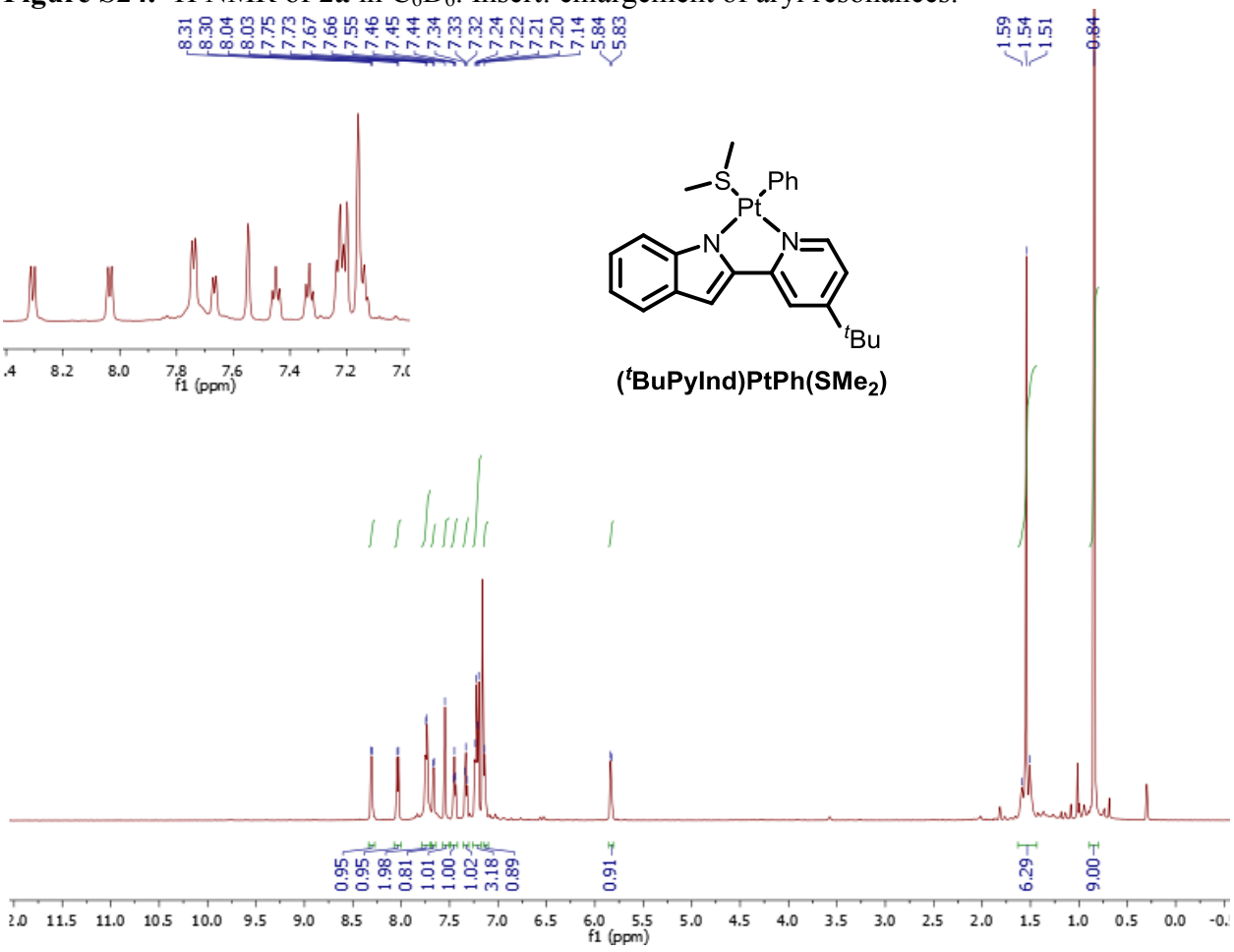


**Figure S25.** $^{13}C\{^{1}H\}$ NMR of **2a** in $C_6D_6$.

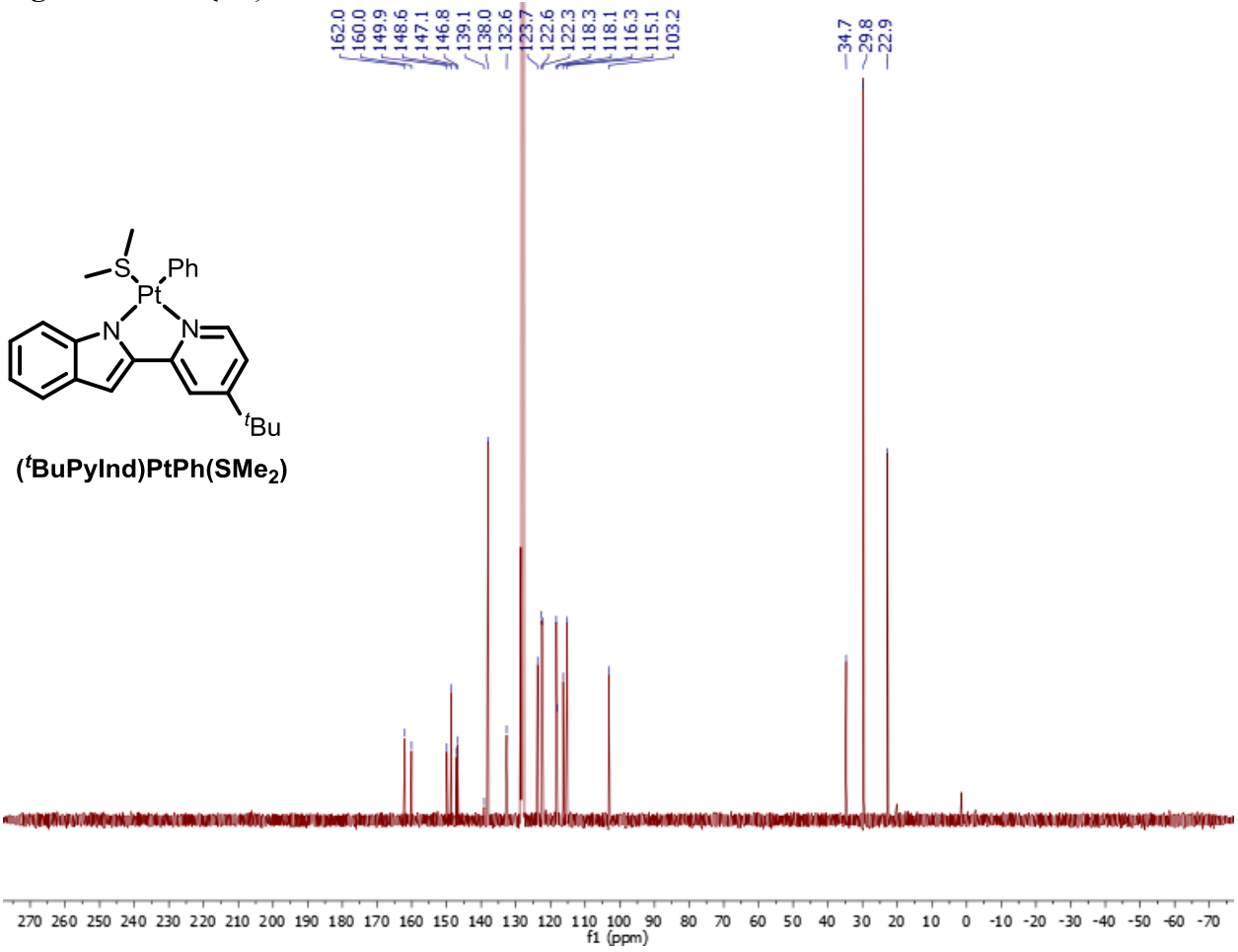


**Figure S26.** $^{1}H$ NMR of **S3b** in $CD_2Cl_2$.

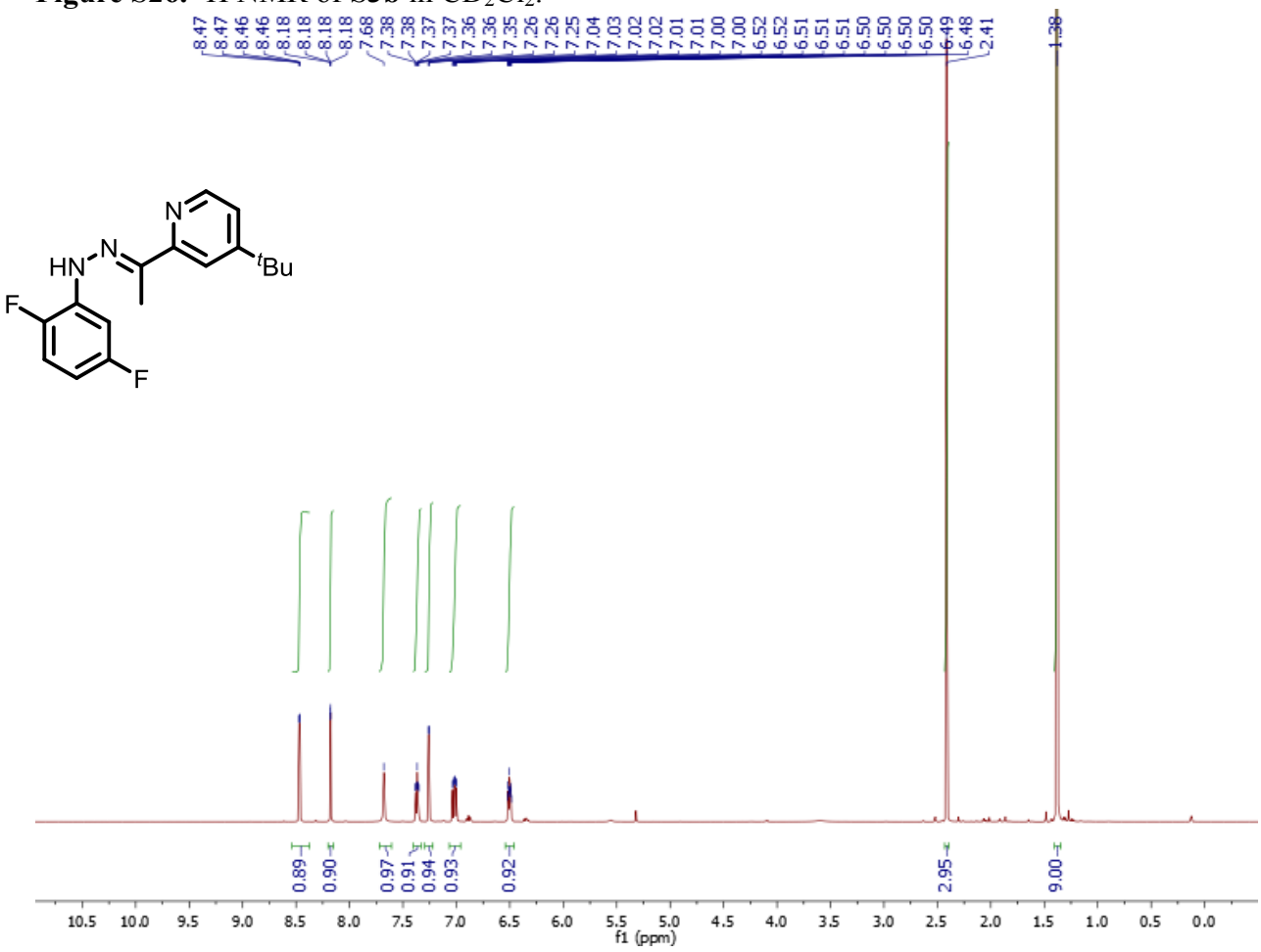


**Figure S27.** $^{13}C\{^{1}H\}$ NMR of **S3b** in $CD_2Cl_2$.

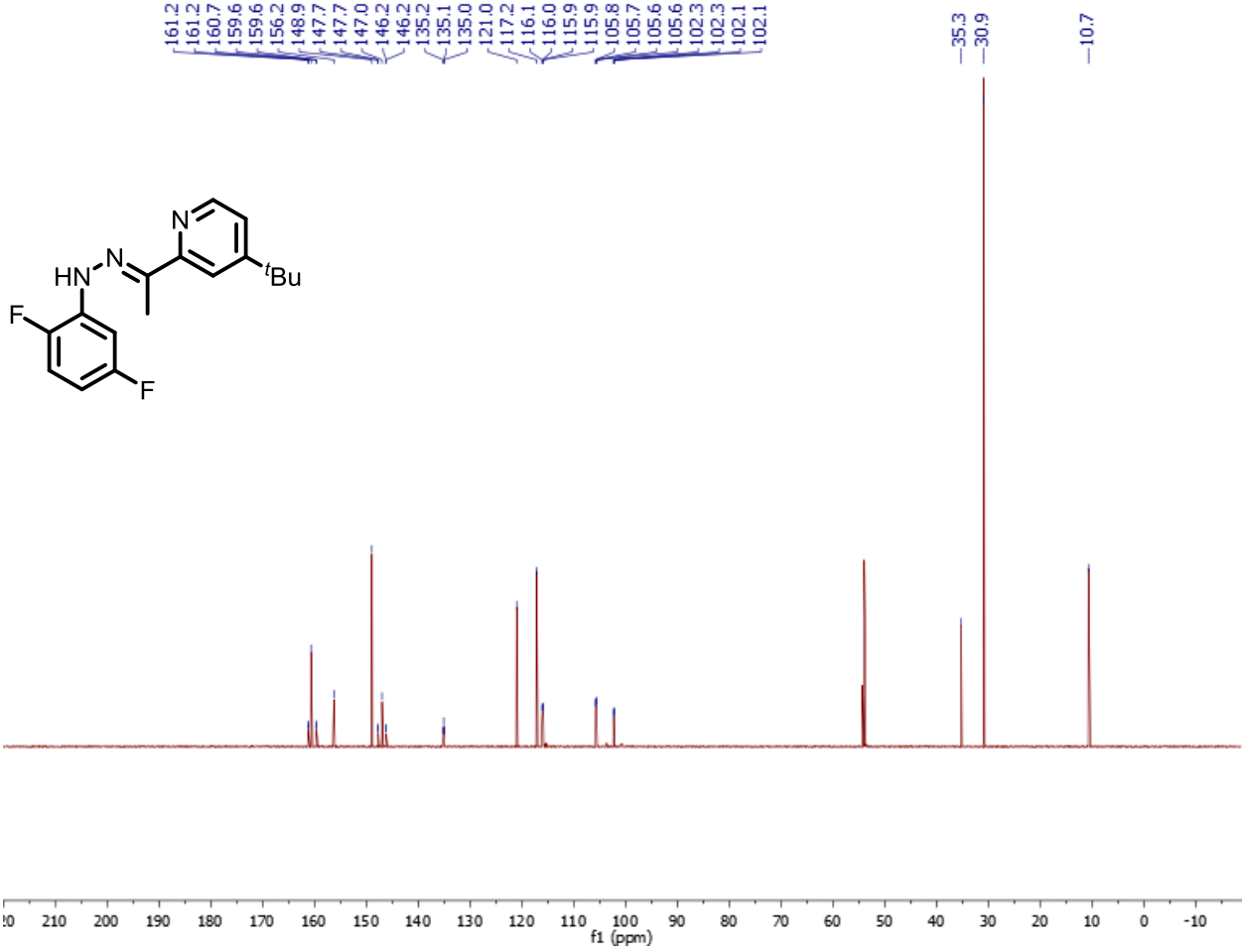


**Figure S28.** $^{19}F$ NMR of **S3b** in $CD_2Cl_2$. Insert: expansion of the ligand based $^{19}F$ resonances.

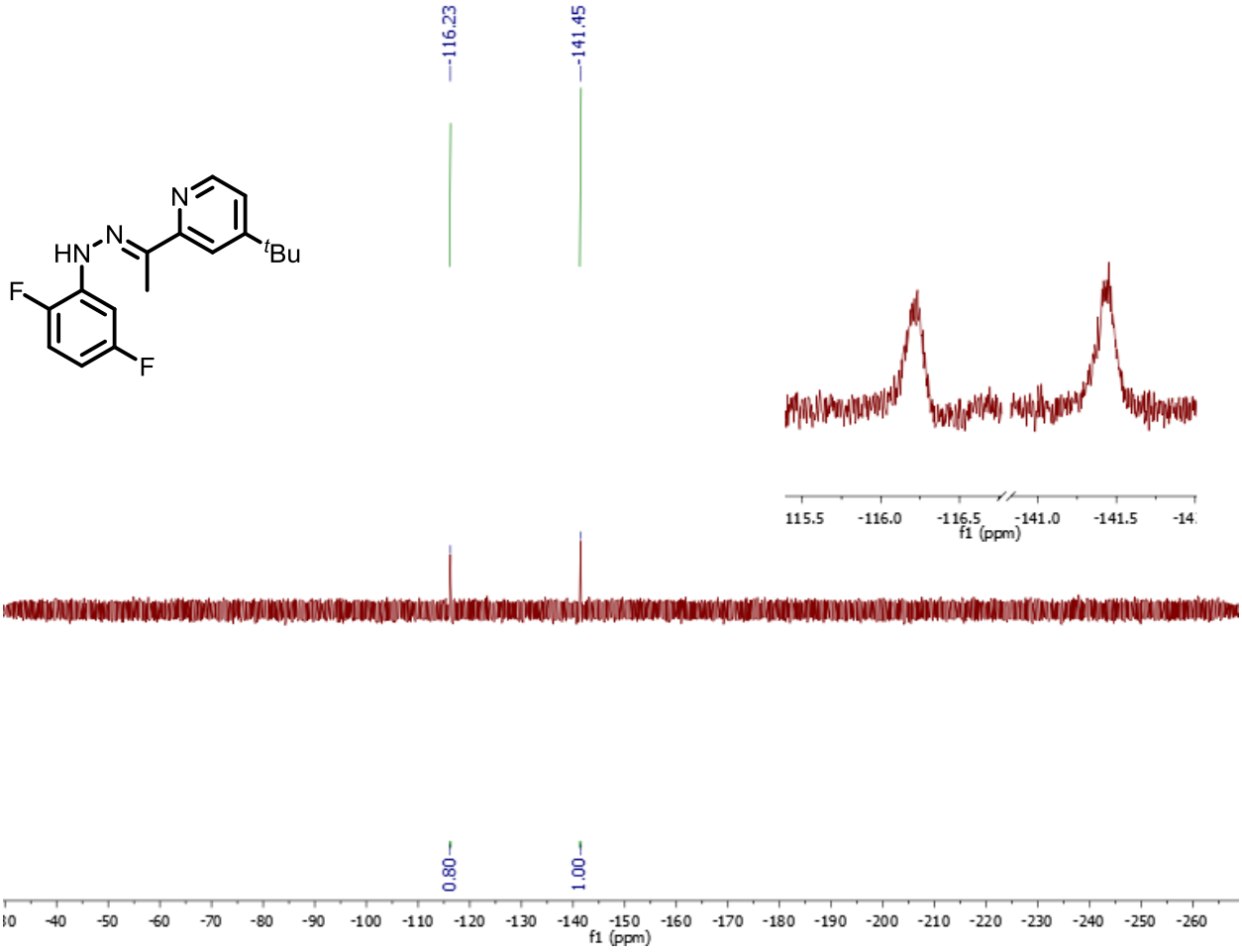


**Figure S29.** $^{1}H$ NMR of **1b** in $CD_2Cl_2$.

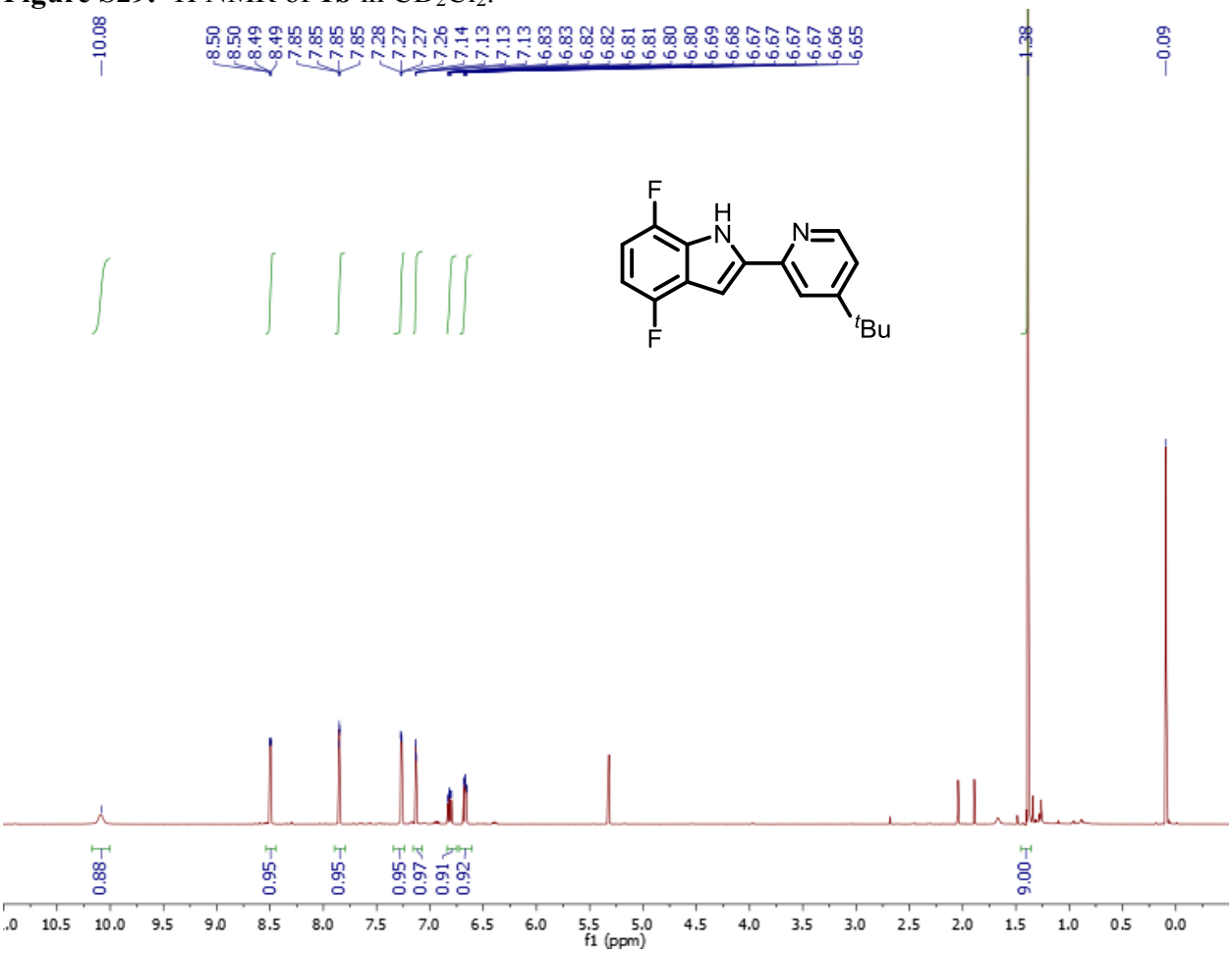


**Figure S30.** $^{13}C\{^{1}H\}$ NMR of **1b** in $CD_2Cl_2$.

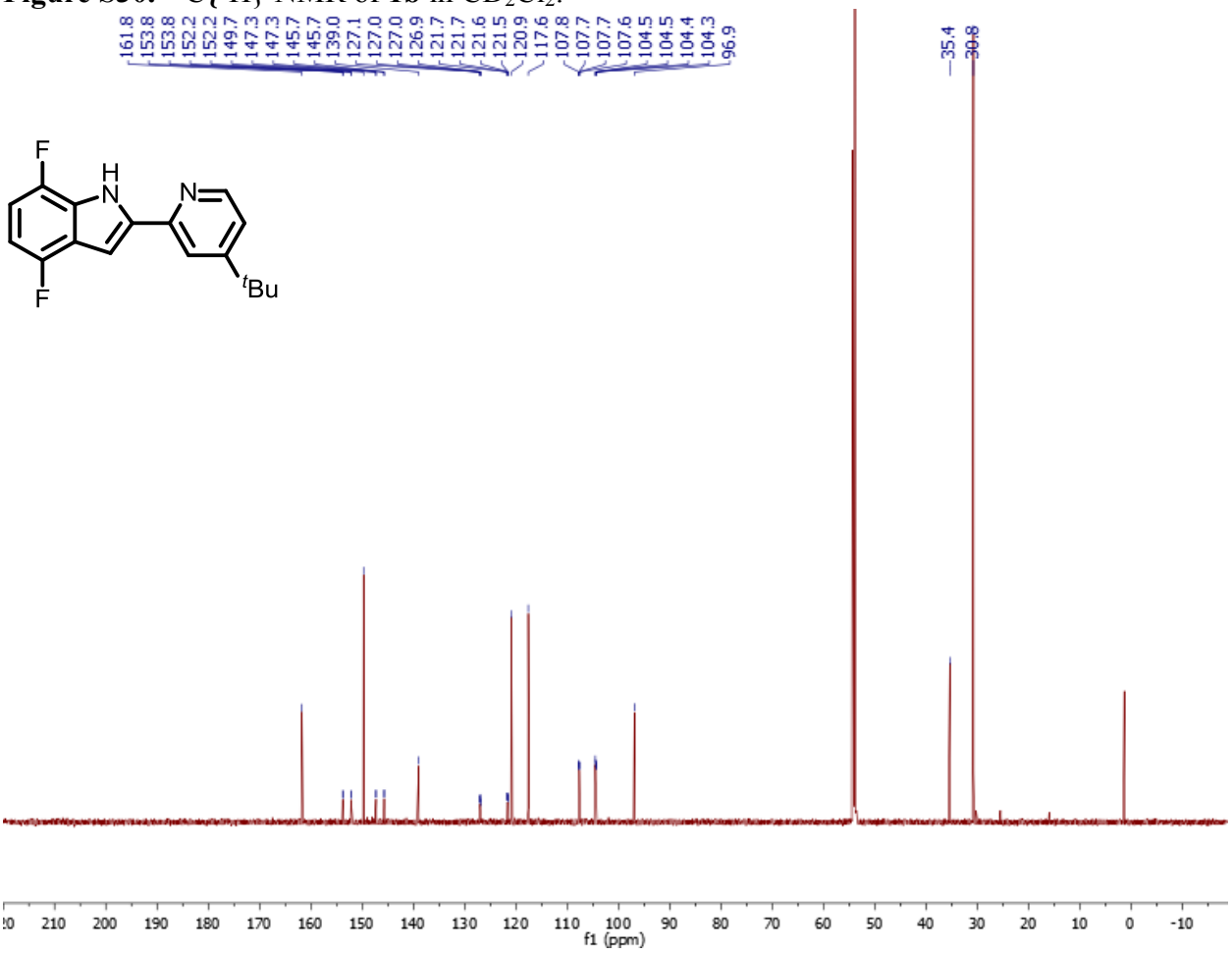


**Figure S31.** $^{19}F$ NMR of **1b** in $CD_2Cl_2$. Insert: expansion of the ligand based $^{19}F$ resonances.

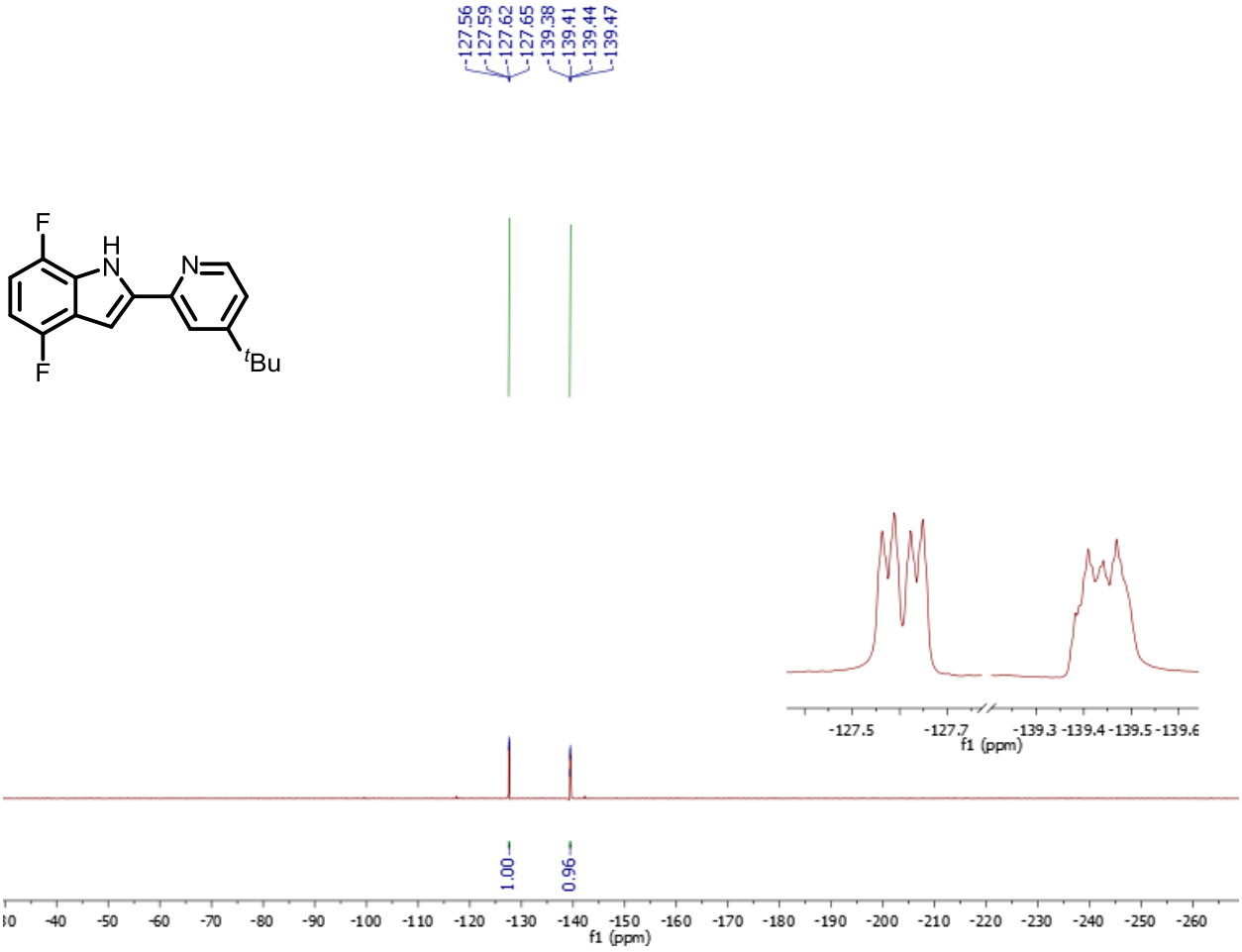
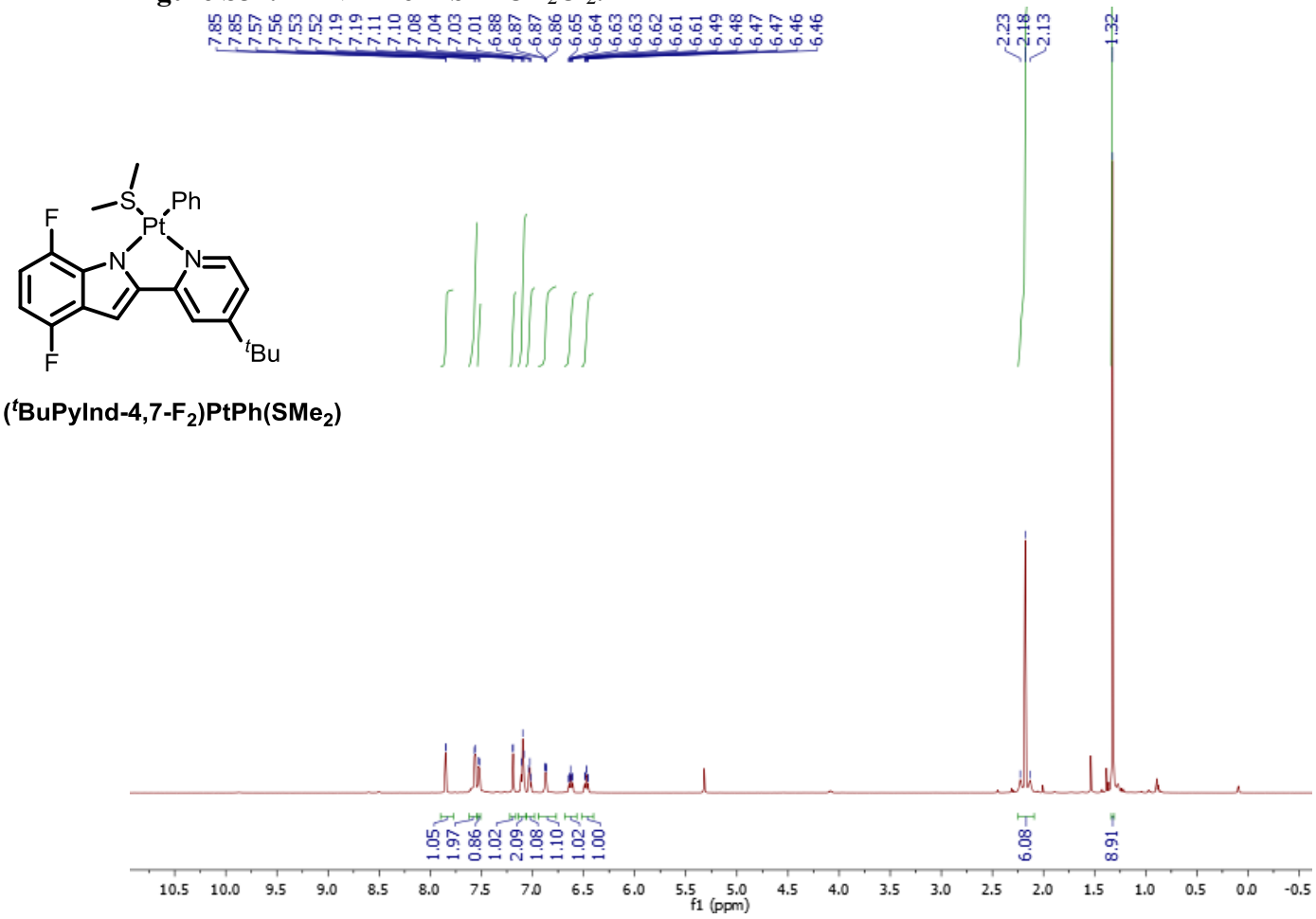


**Figure S32.** $^{1}$H NMR of **2b** in $CD_2Cl_2$.




($^{t}$BuPyInd-4,7-$F_2$)PtPh($SMe_2$)

**Figure S33.** $^{13}C\{^{1}H\}$ NMR of **2b** in $CD_2Cl_2$.

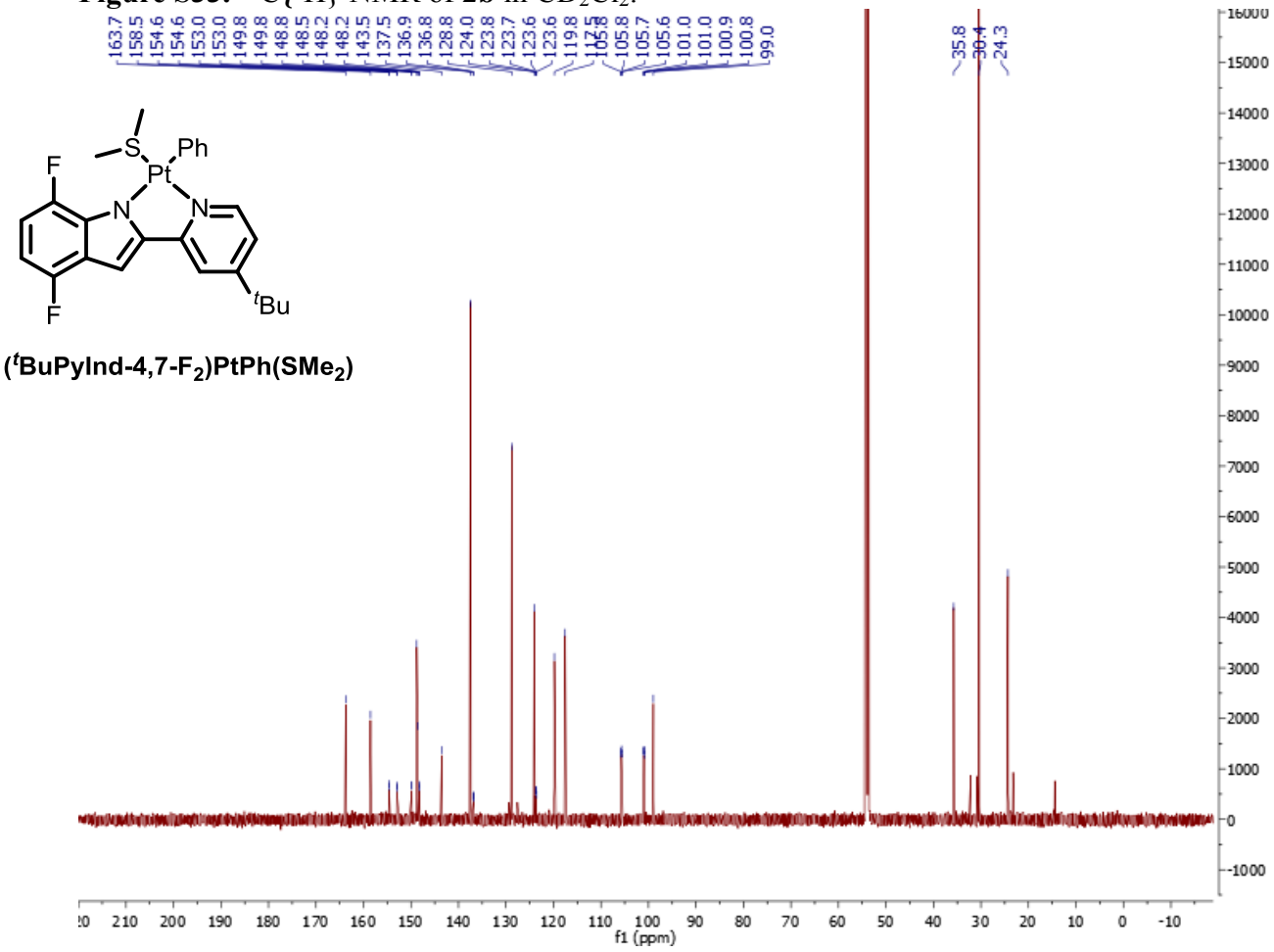
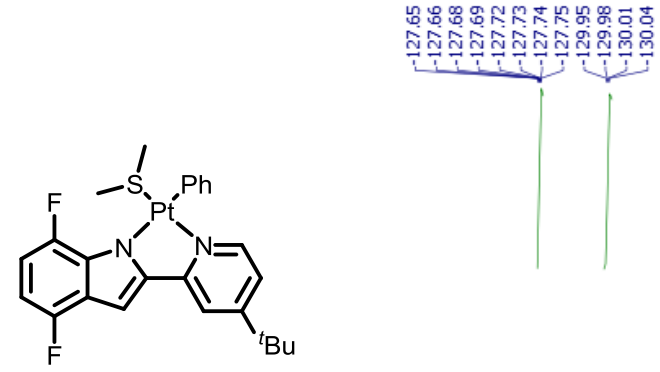


**Figure S34.** $^{19}F$ NMR of **2b** in $CD_2Cl_2$. Insert: expansion of the ligand based $^{19}F$ resonances.




**($^{t}$BuPyInd-4,7-$F_2$)PtPh($SMe_2$)**

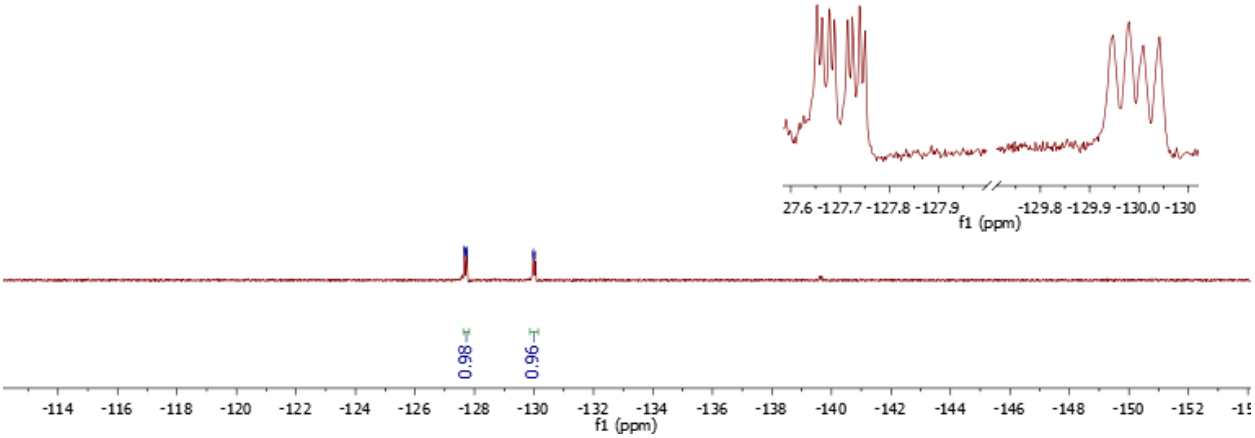


**Figure S35**. $^{1}H$ NMR of **S3c** in $CD_2Cl_2$.

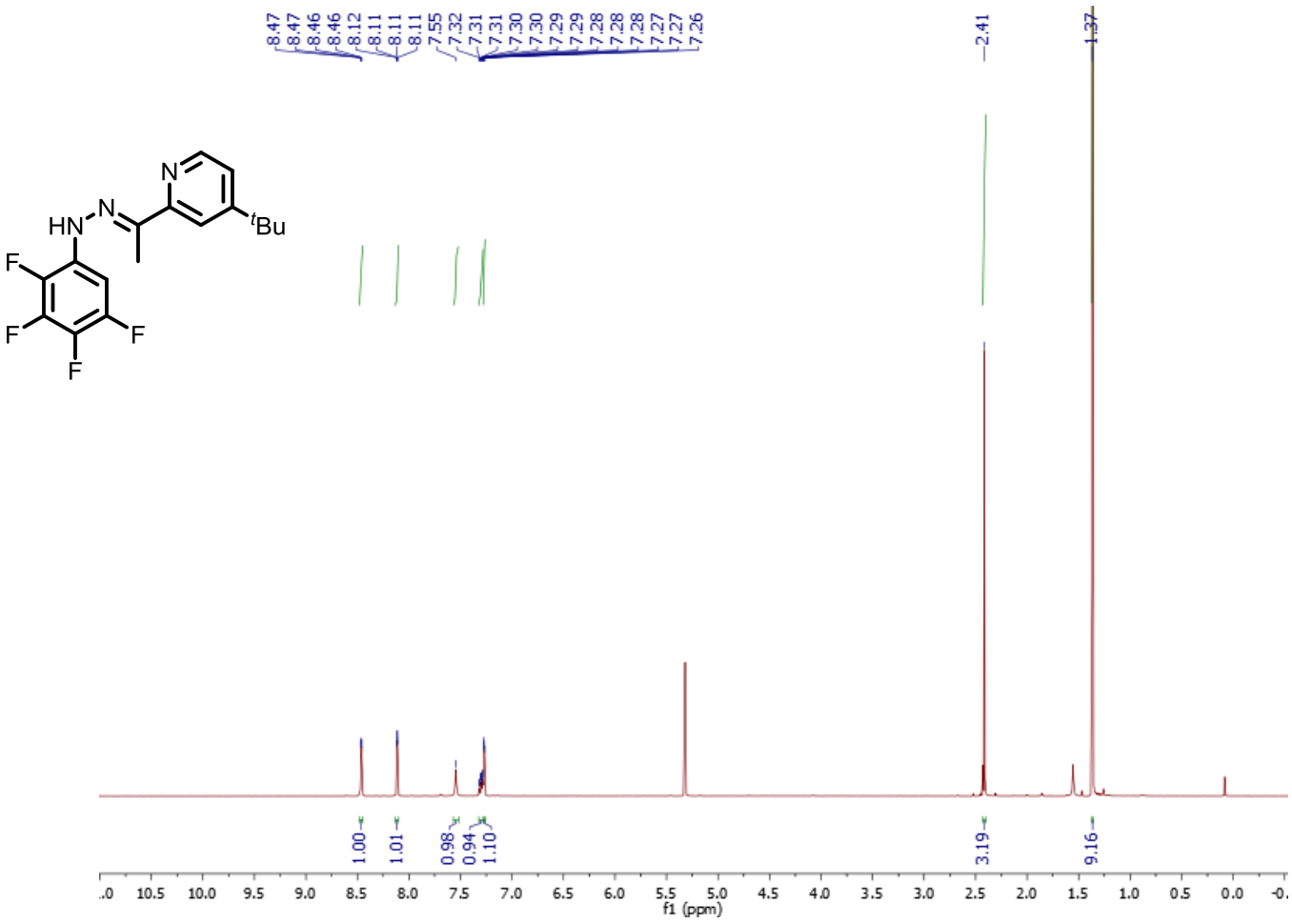


**Figure S36**. $^{13}C\{^{1}H\}$ NMR of **S3c** in $CD_2Cl_2$. Insert: expansion of arene carbons coupling to $^{19}F$.

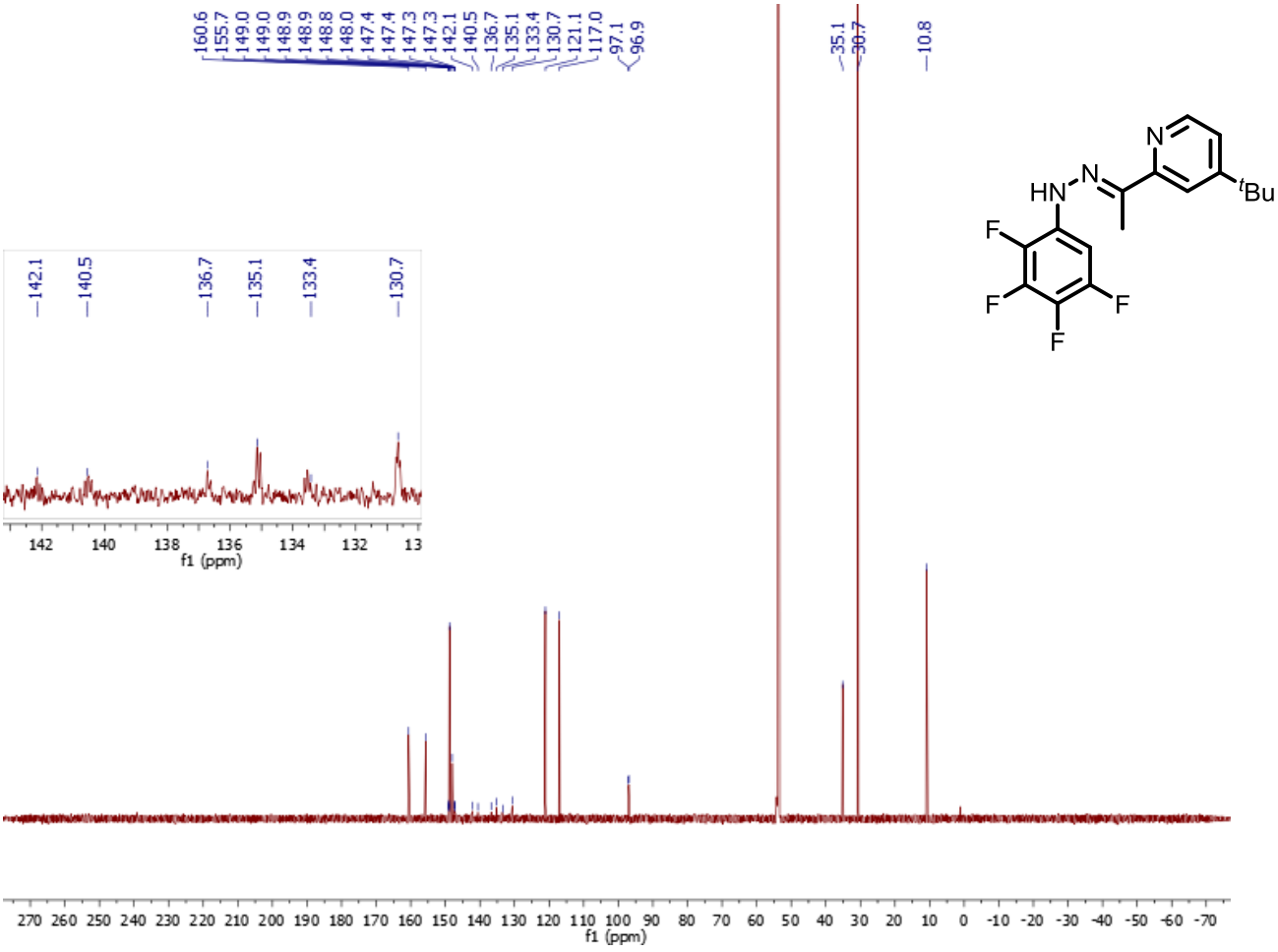


**Figure S37**. $^{19}F$ NMR of **S3c** in $CD_2Cl_2$. Left insert: expansion of $^{19}F$ resonance centered at -139.5 ppm. Right insert: expansion of $^{19}F$ resonances centered at -157.7, -162.9, and -170.6 ppm.

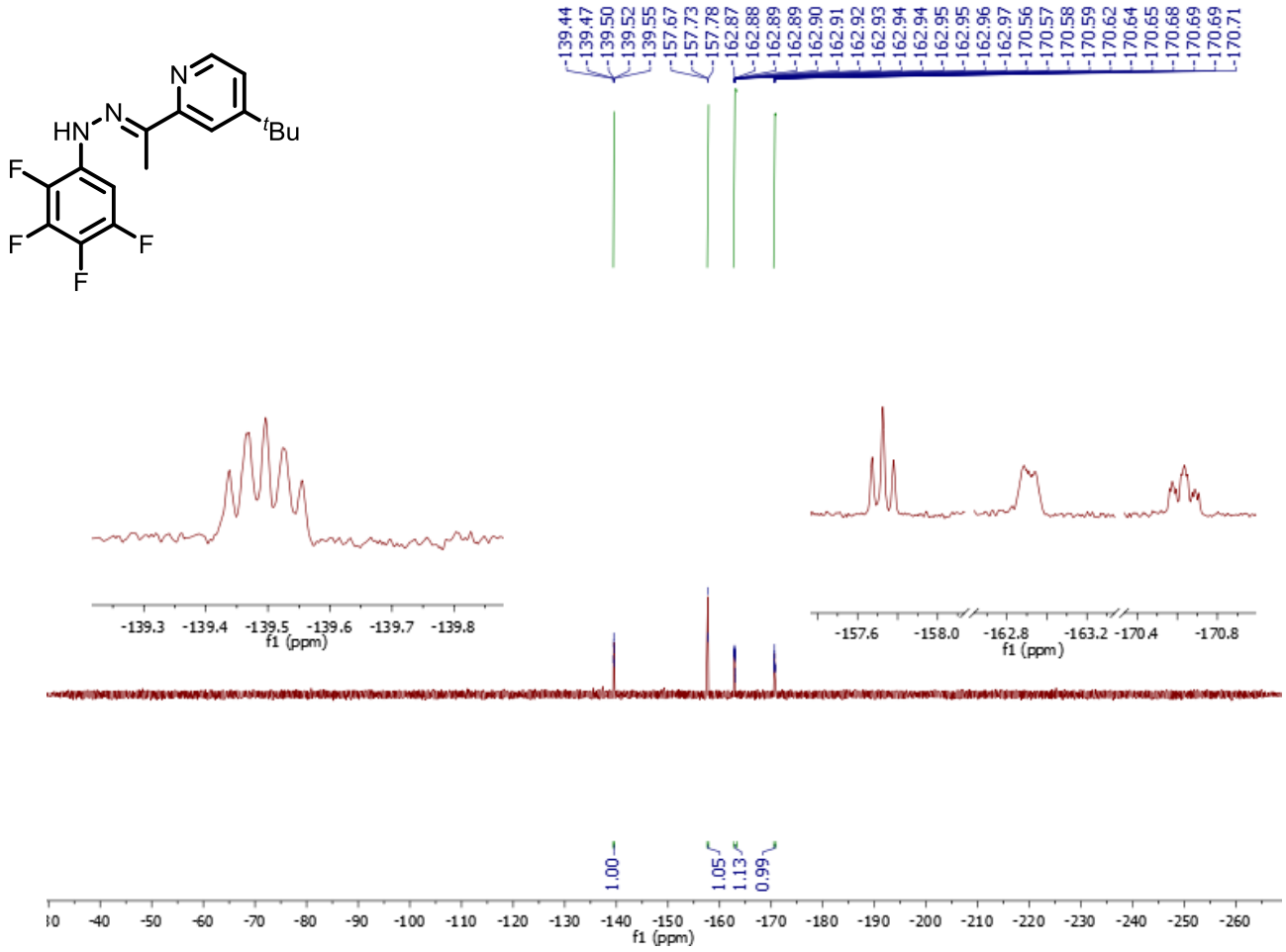


**Figure S38**. $^{1}H$ NMR of **1c** in $CD_2Cl_2$.

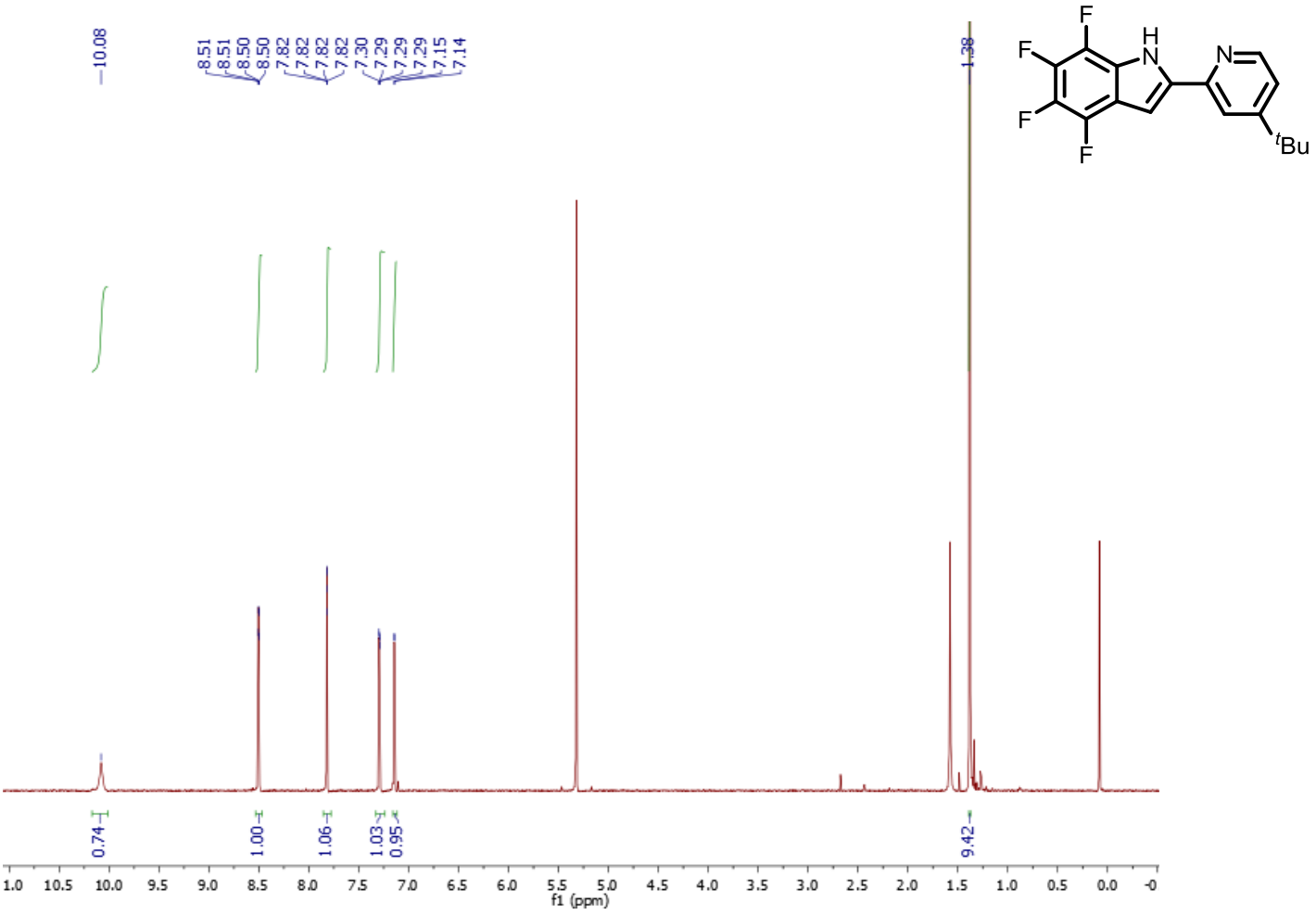


**Figure S39**. $^{13}C\{^{1}H\}$ NMR of **1c** in $CD_2Cl_2$. Insert: expansion of arene carbons coupling to $^{19}F$.

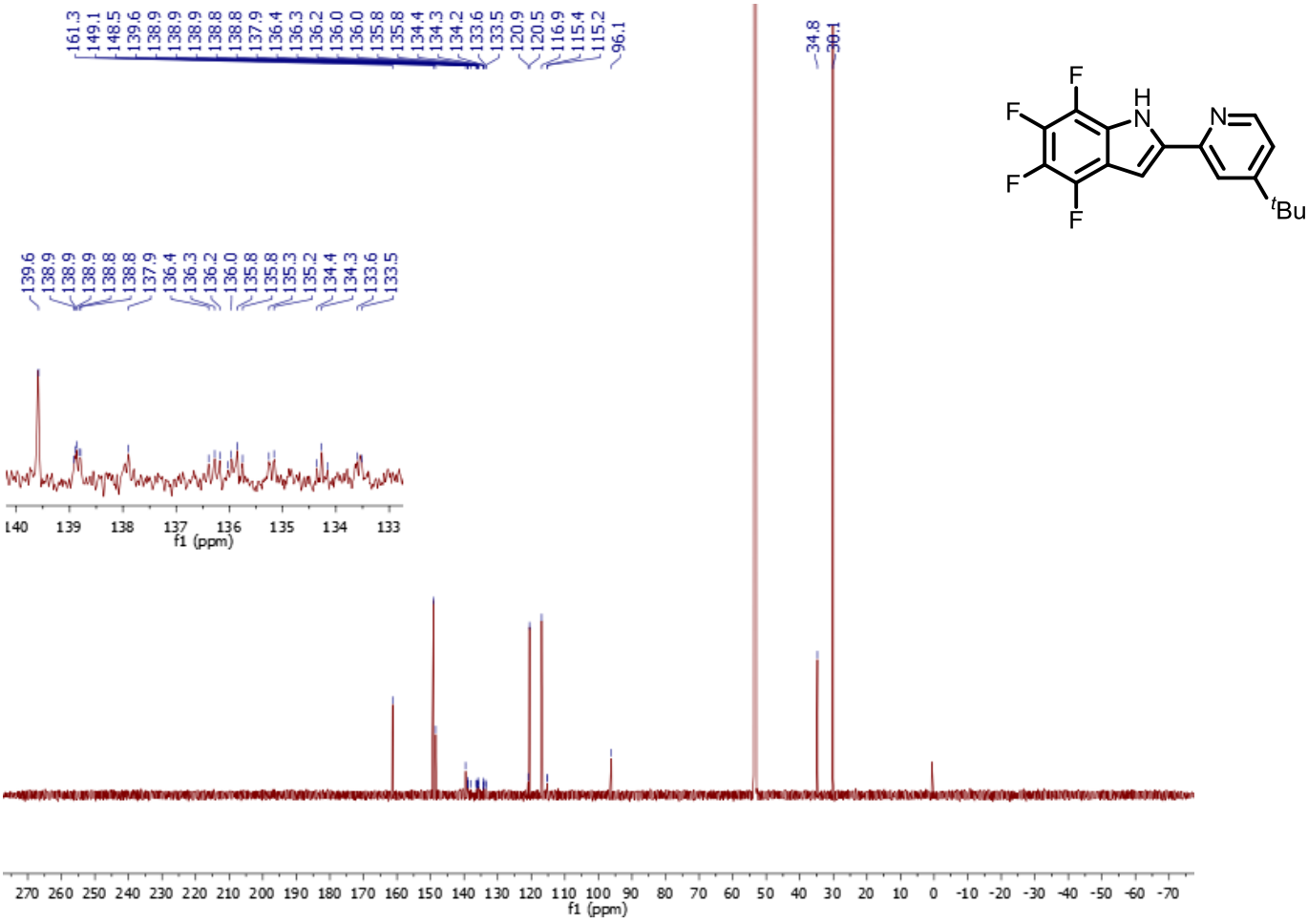


**Figure S40**. $^{19}F$ NMR of **1c** in $CD_2Cl_2$. Left insert: expansion of $^{19}F$ resonance centered at -150.1 ppm. Right insert: expansion of $^{19}F$ resonances centered at -160.8, -165.1, and -169.6 ppm.

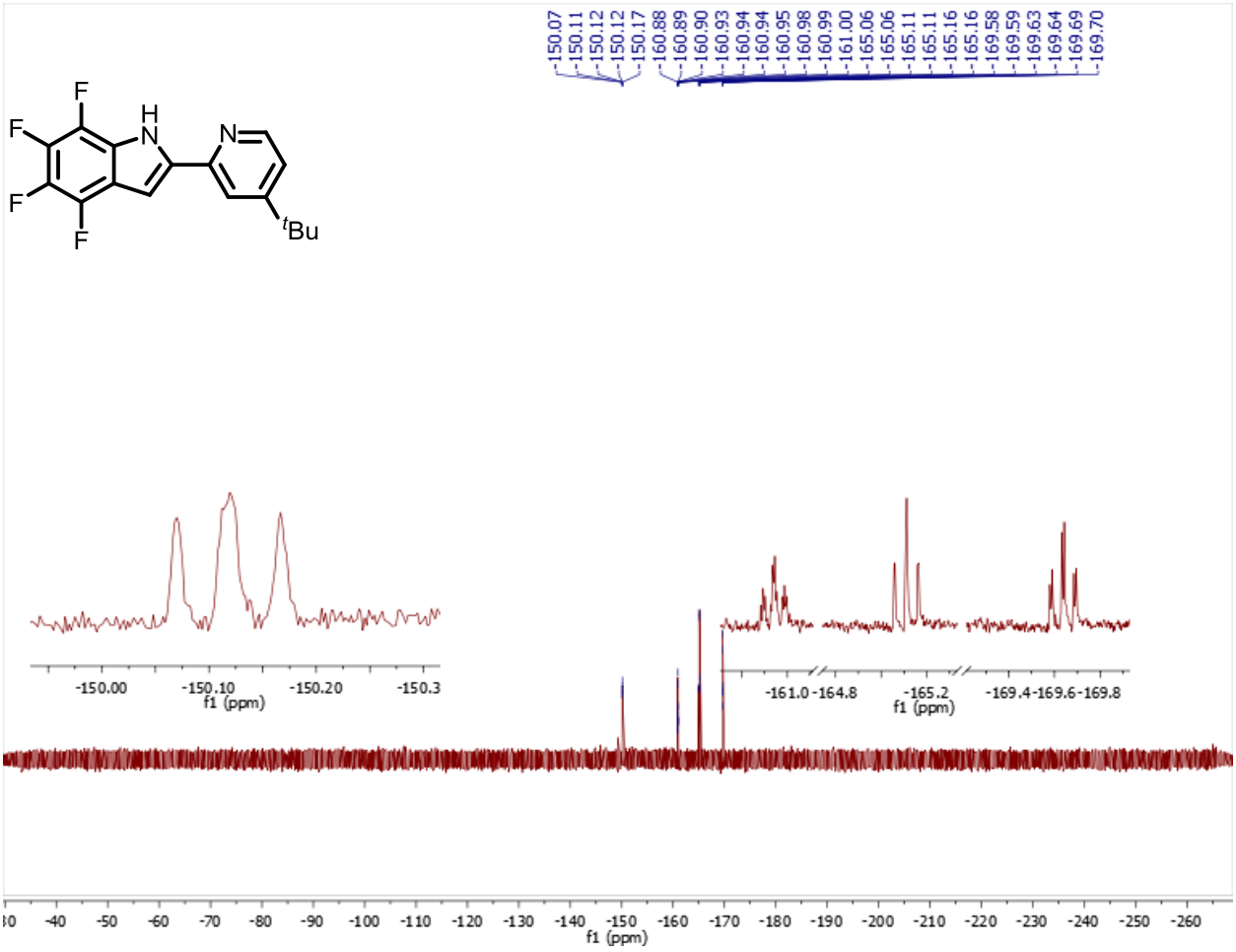


**Figure S41**. $^{1}$H NMR of **2c** in $C_6D_6$.

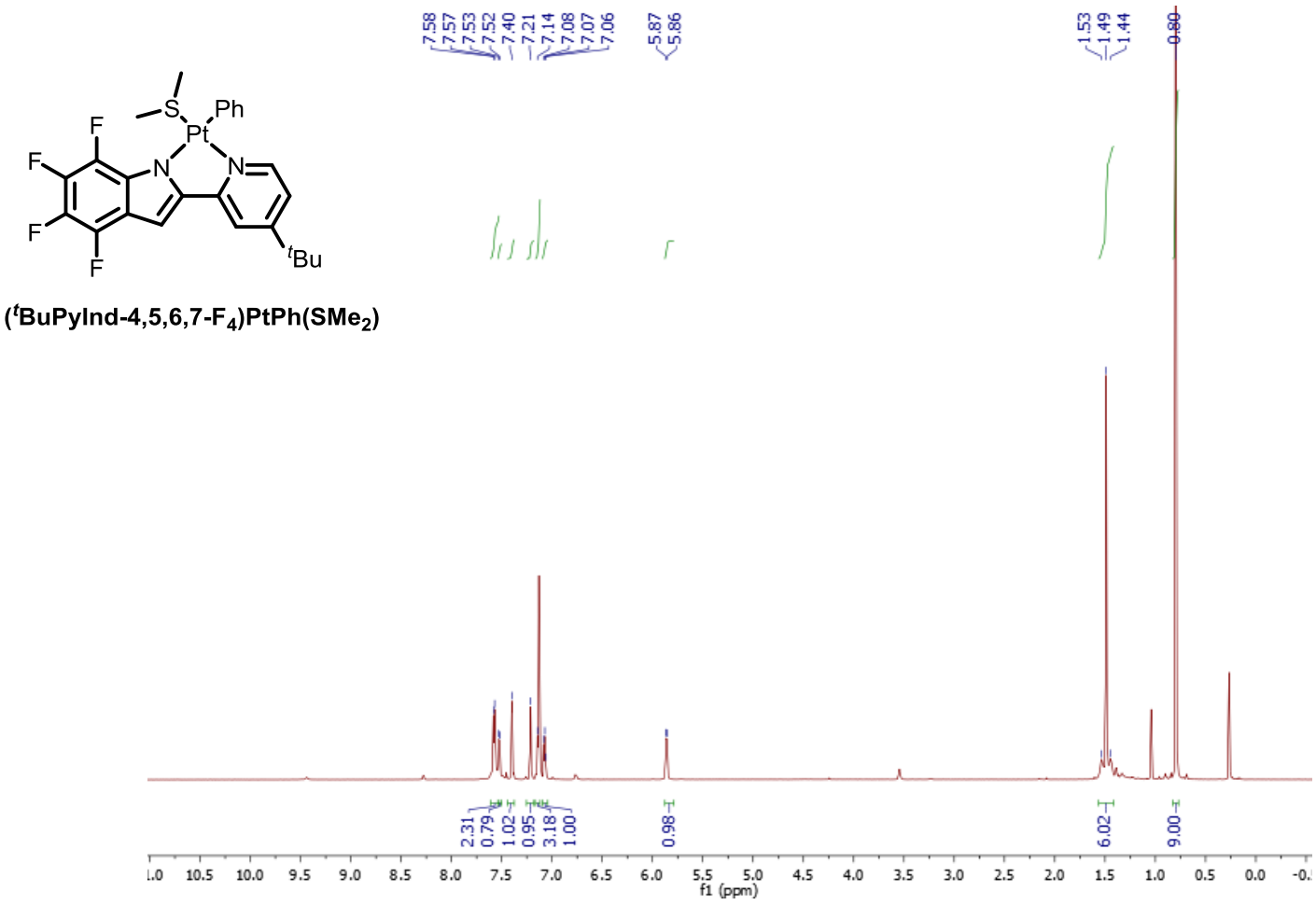


**Figure S42**. $^{13}C\{^{1}H\}$ NMR of **2c** in $C_6D_6$. expansion of arene carbons coupling to $^{19}F$.

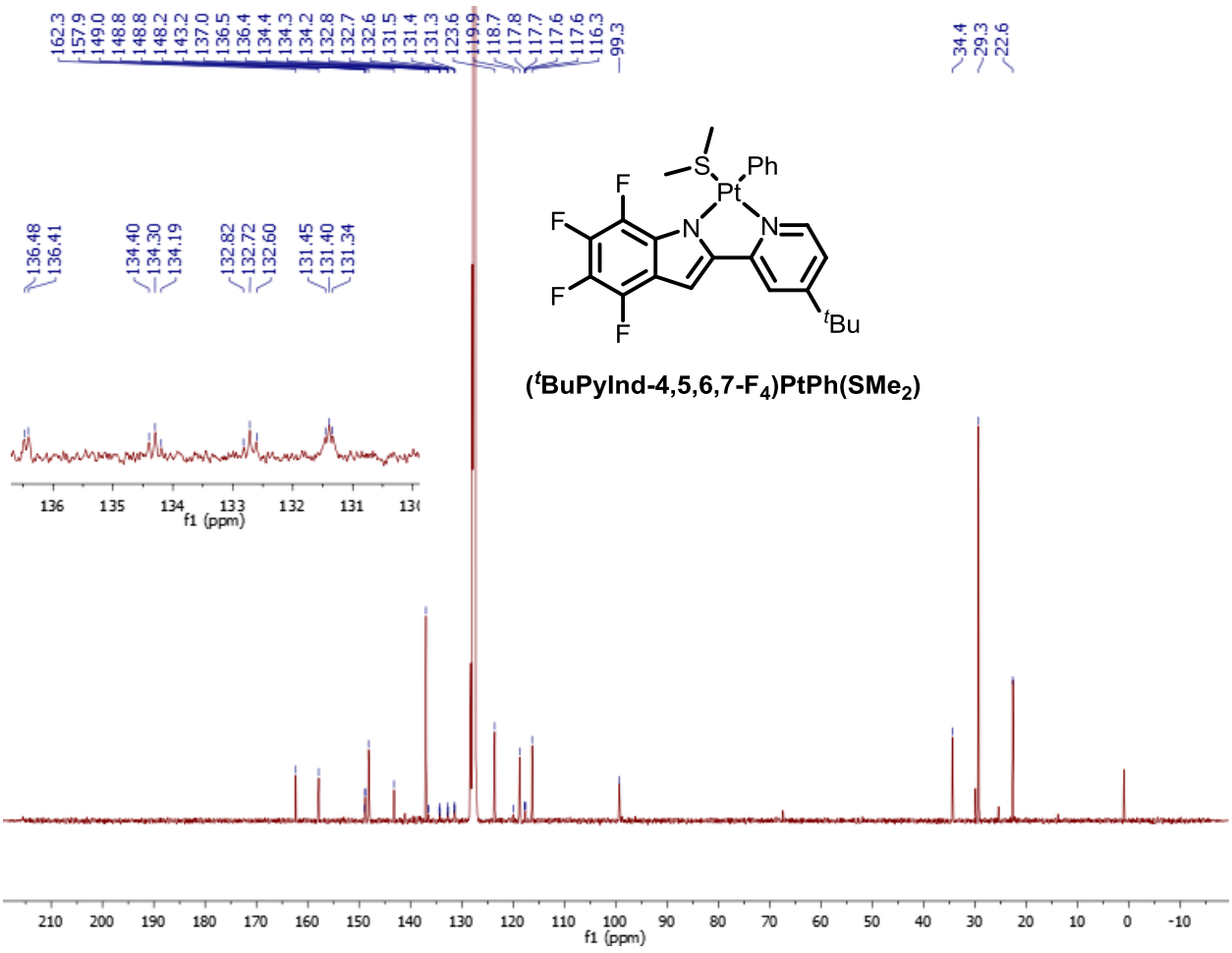


**Figure S43**. $^{19}F$ NMR of **2c** in $C_6D_6$. Left insert: expansion of $^{19}F$ resonances centered at -151.7 and -153.4 ppm. Right insert: expansion of $^{19}F$ resonances centered at -169.3 and -173.5 ppm.

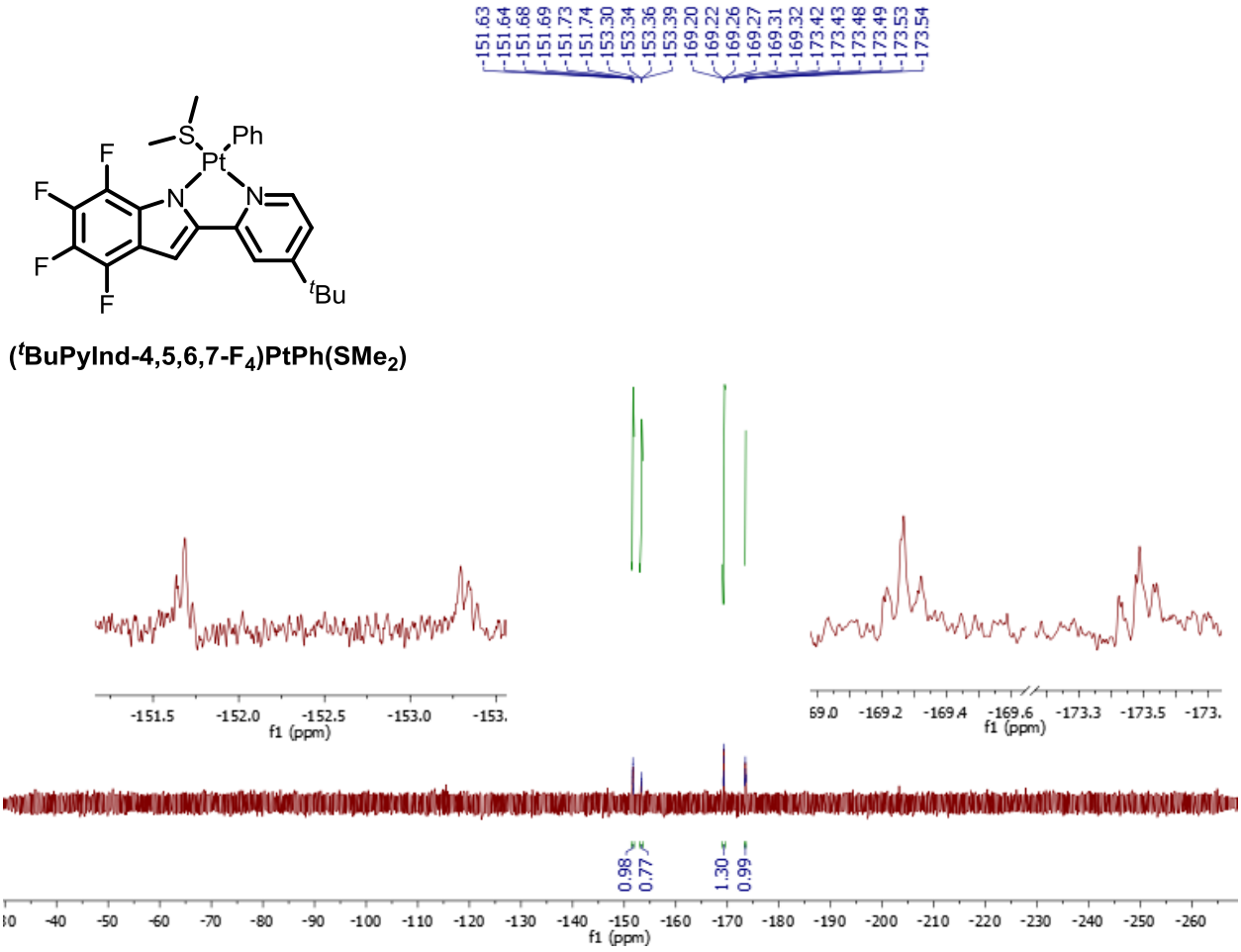


**Figure S44**. $^{1}$H NMR of **S3d** in DMSO-$d_6$.

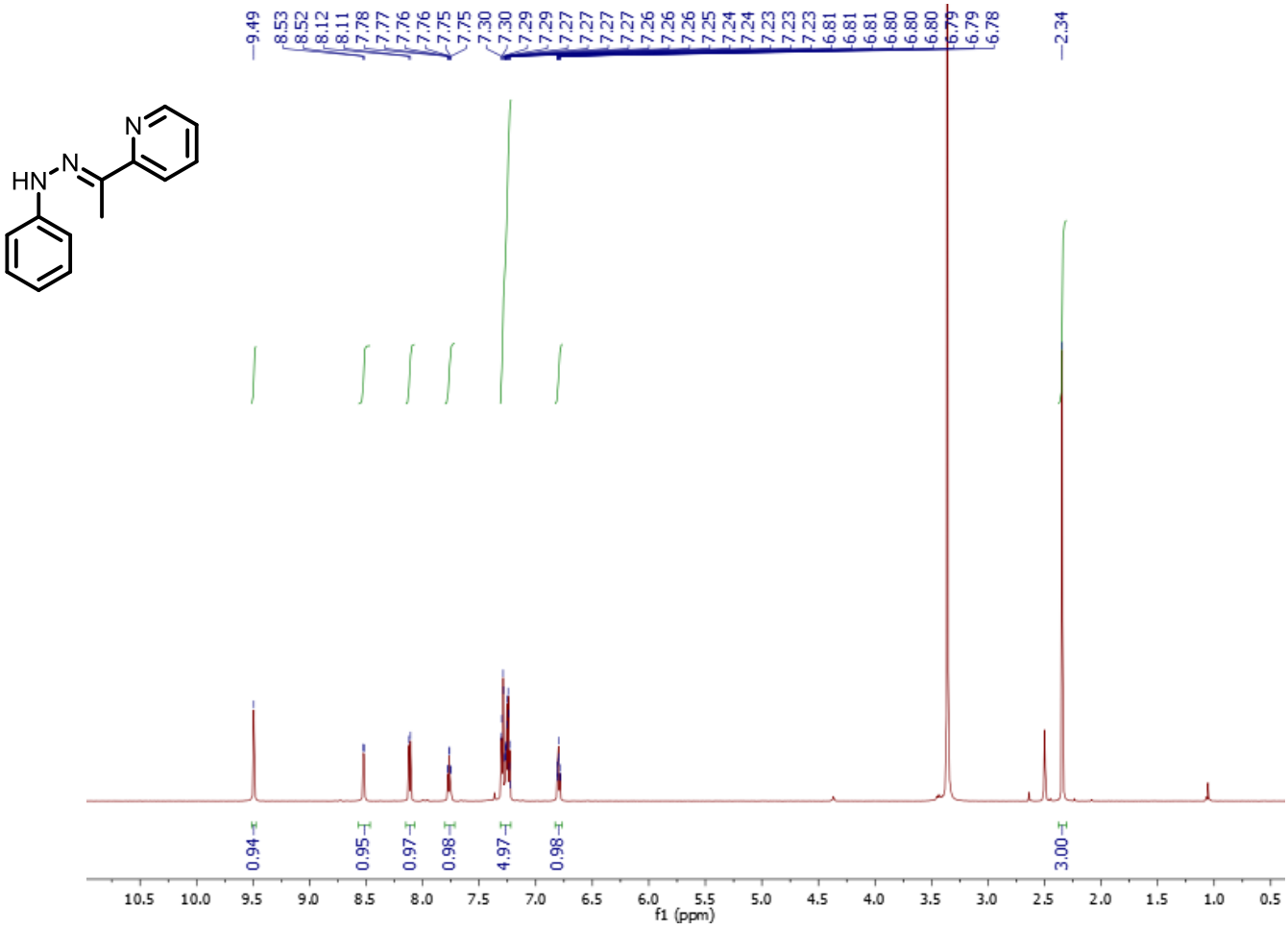


**Figure S45**. $^{13}C\{^{1}H\}$ NMR of **S3d** in DMSO-$d_6$.

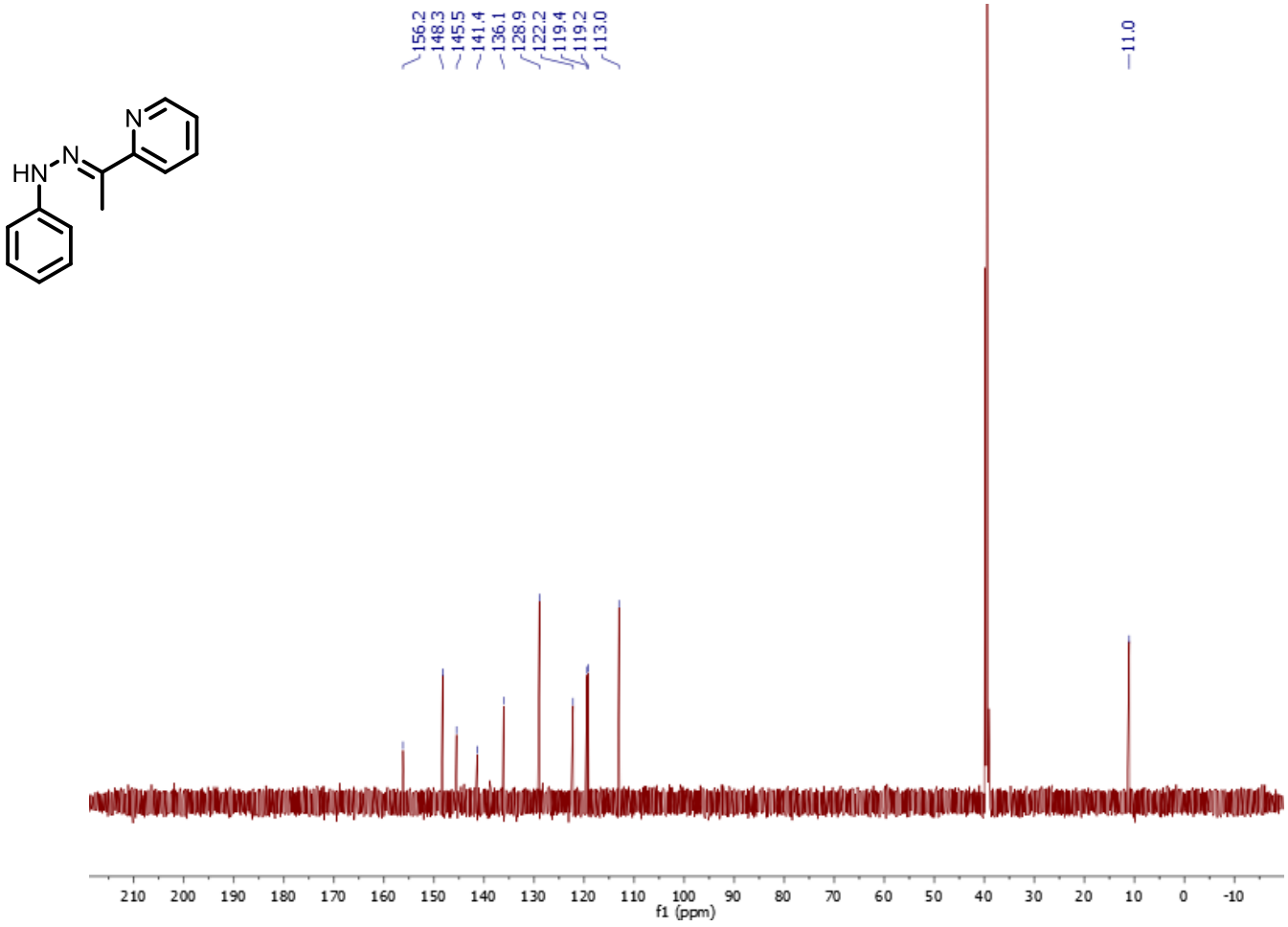


**Figure S46**. $^{1}H$ NMR of **1d** in $CD_2Cl_2$.

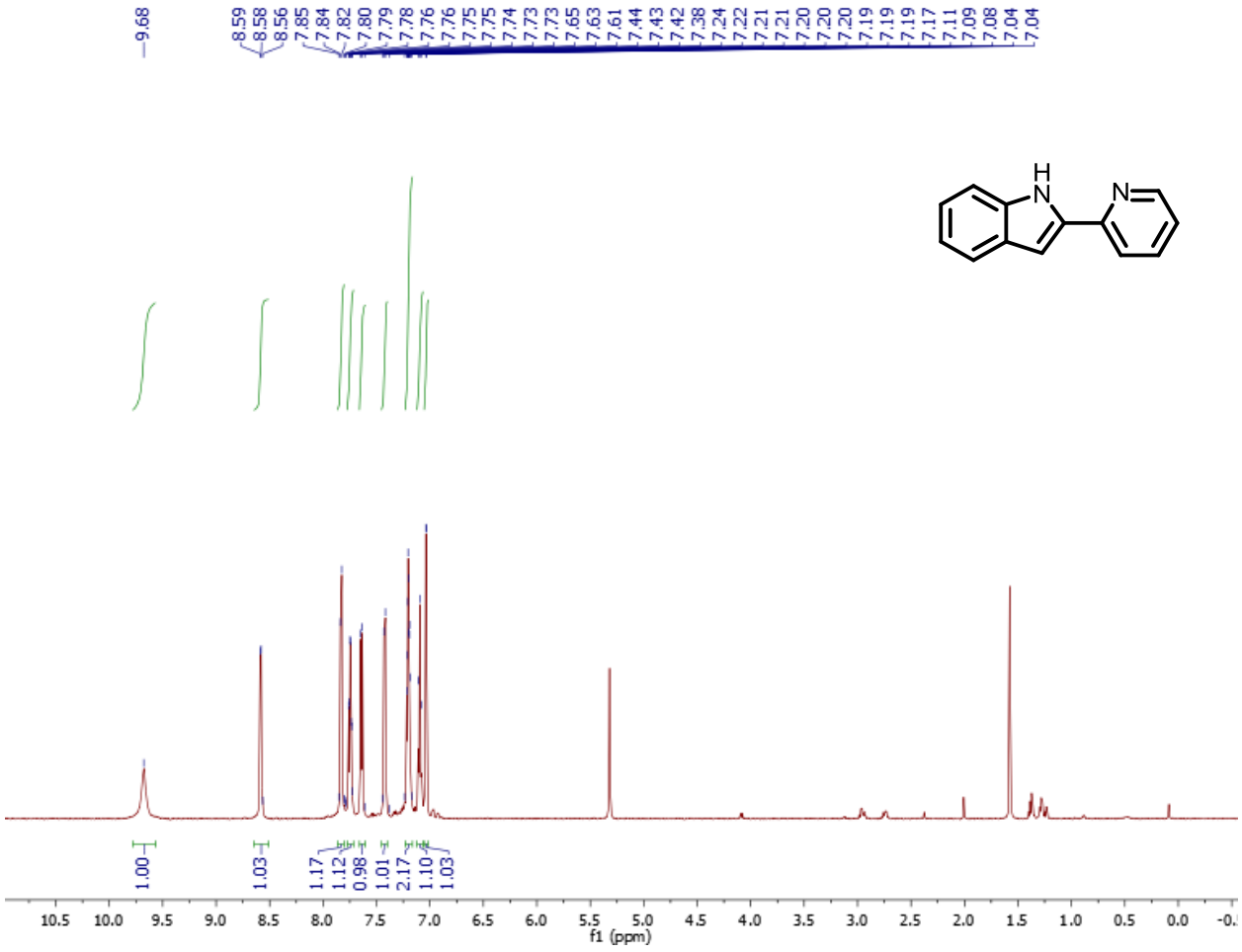


**Figure S47**. $^{13}C\{^{1}H\}$ NMR of **1d** in $CD_2Cl_2$.

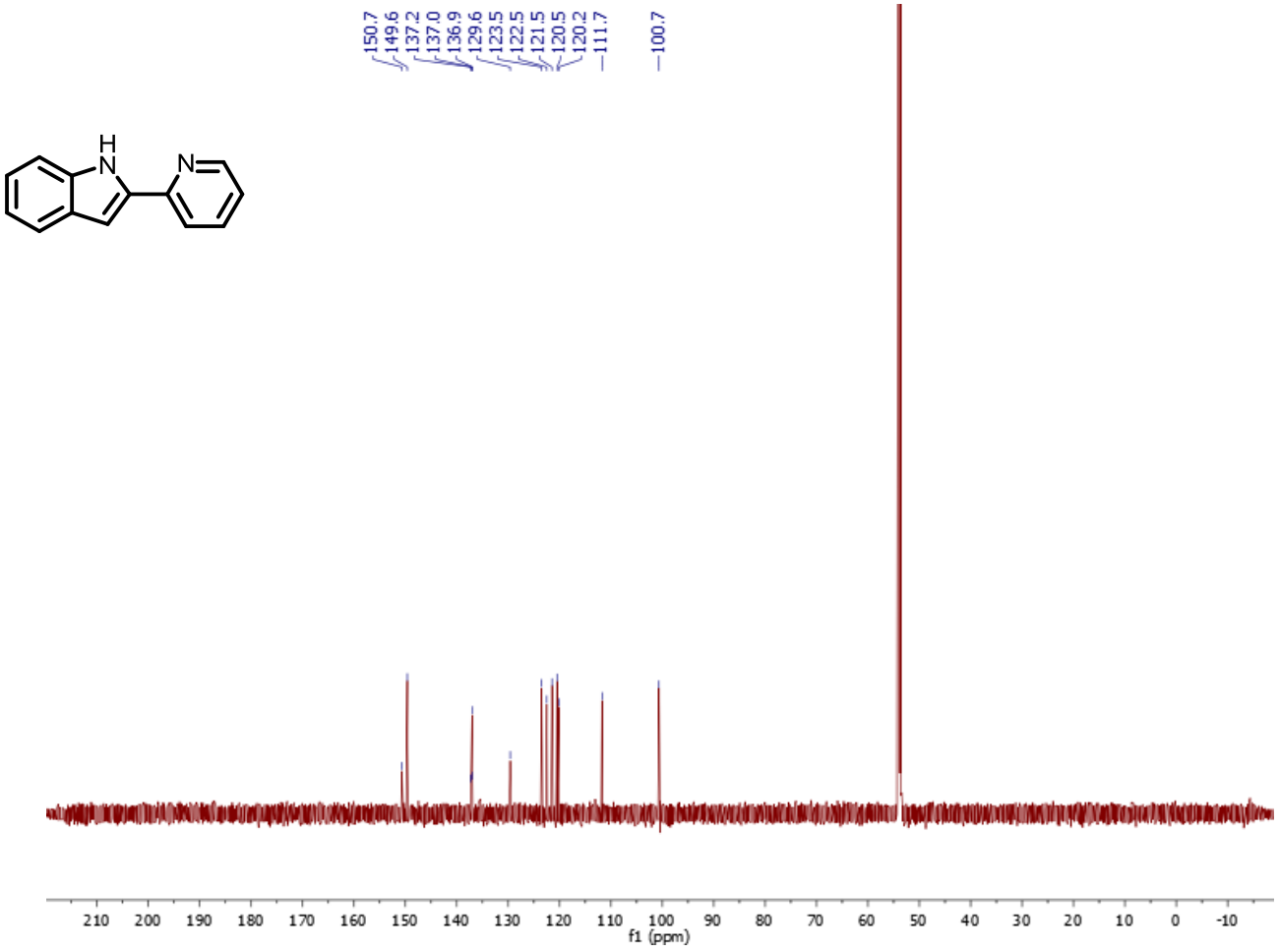


**Figure S48**. $^{1}H$ NMR of **2d** in $CD_2Cl_2$.

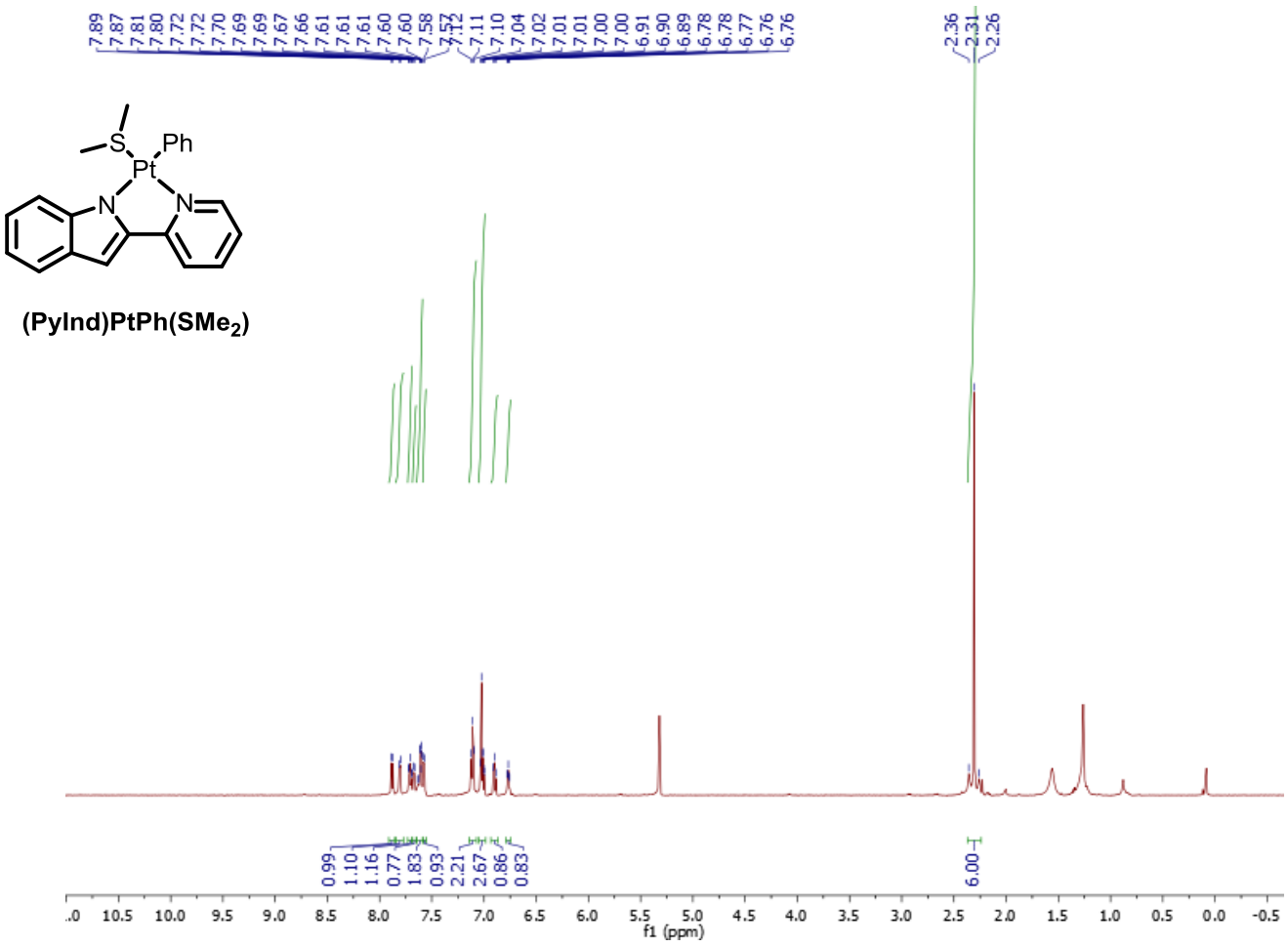


**Figure S49**. $^{13}C\{^{1}H\}$ NMR of **2d** in $CD_2Cl_2$. Insert: expansion from 165.0 to 130.0 ppm.

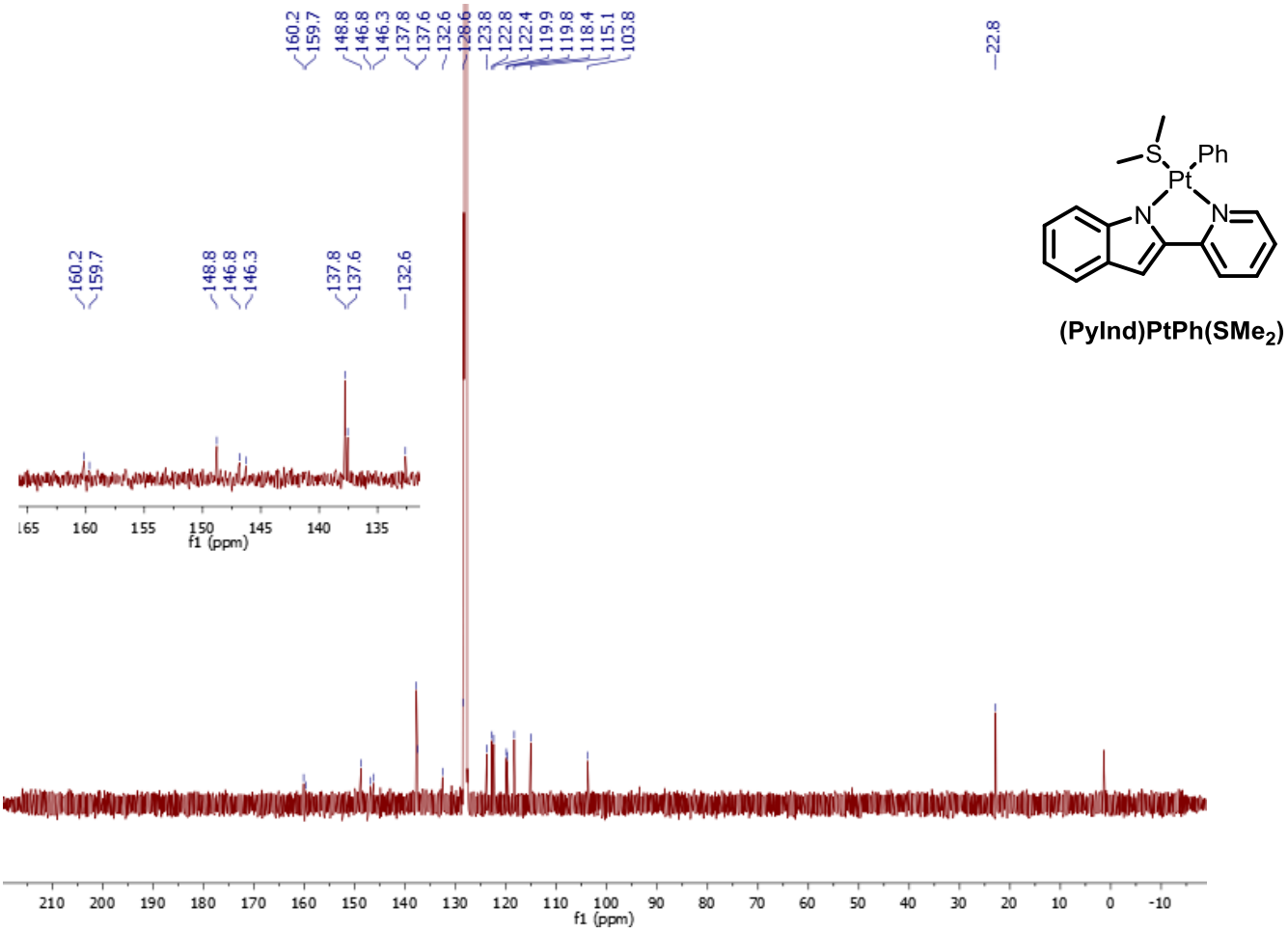


**Figure S50**. $^{1}$H NMR of **S3e** in DMSO-$d_6$.

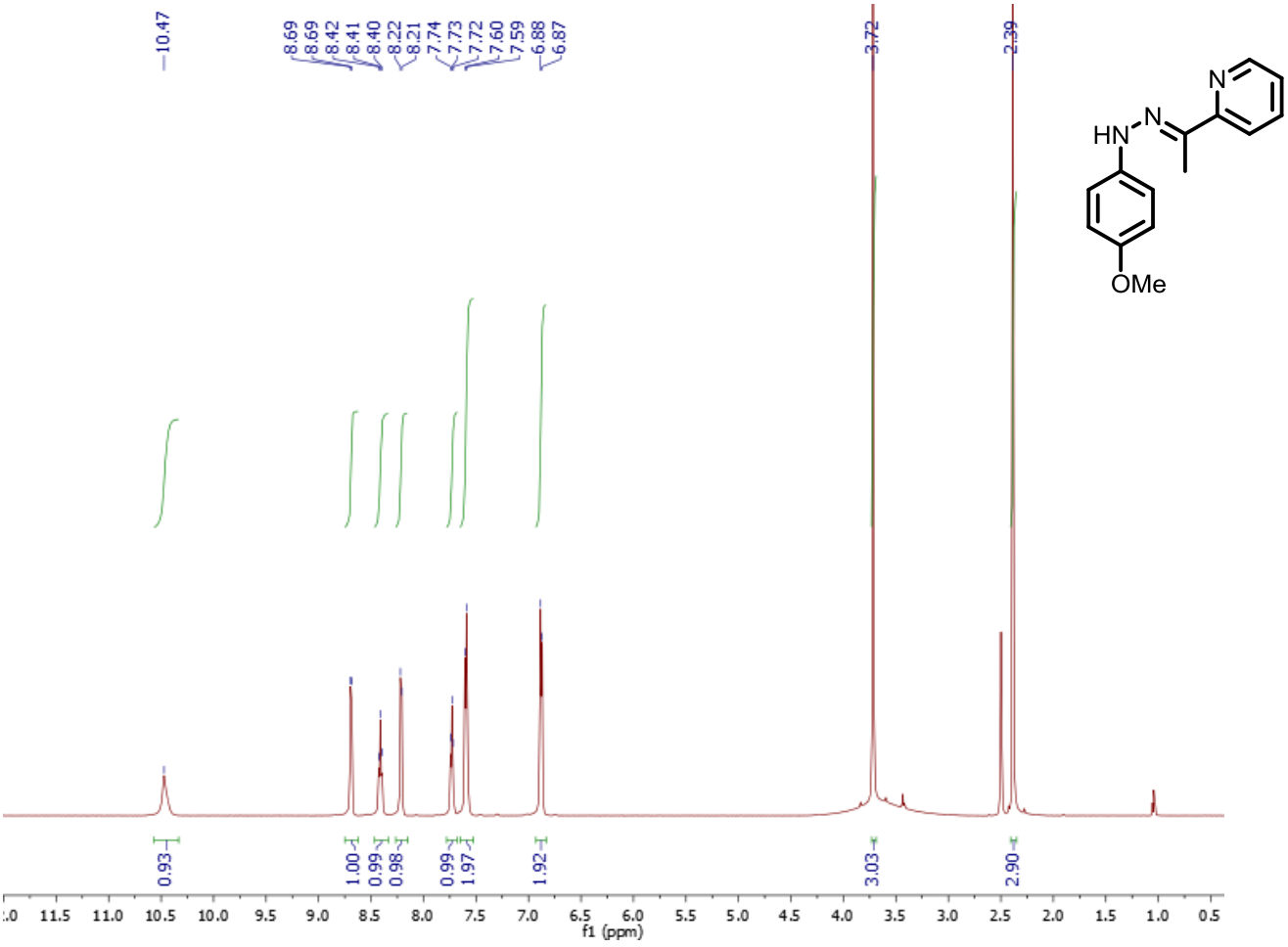


**Figure S51**. $^{13}C\{^{1}H\}$ NMR of **S3e** in DMSO-$d_6$. Insert: expansion from -152.0 ppm to -128.0 ppm.

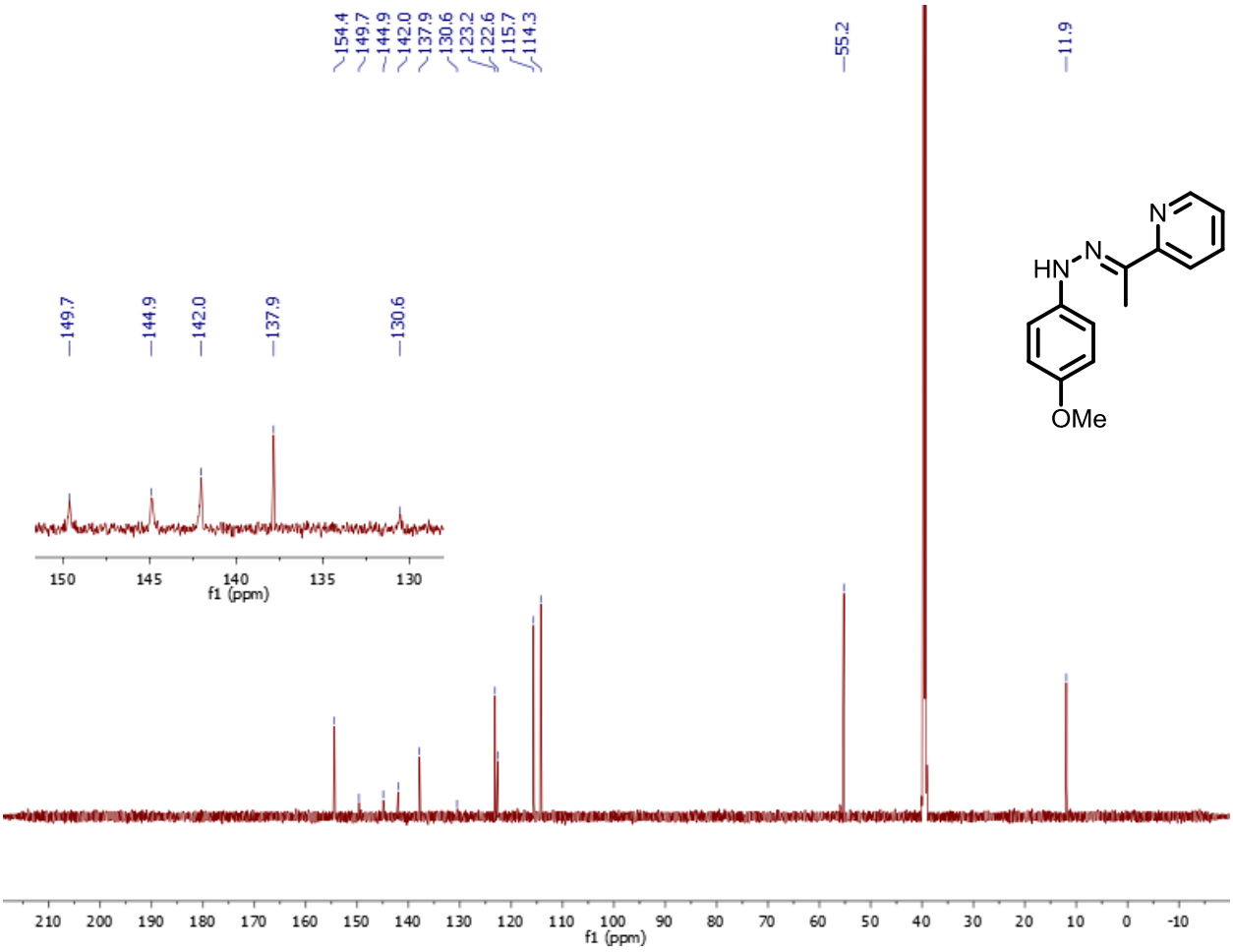


**Figure S52**. $^{1}H$ NMR of **1e** in $CD_2Cl_2$.

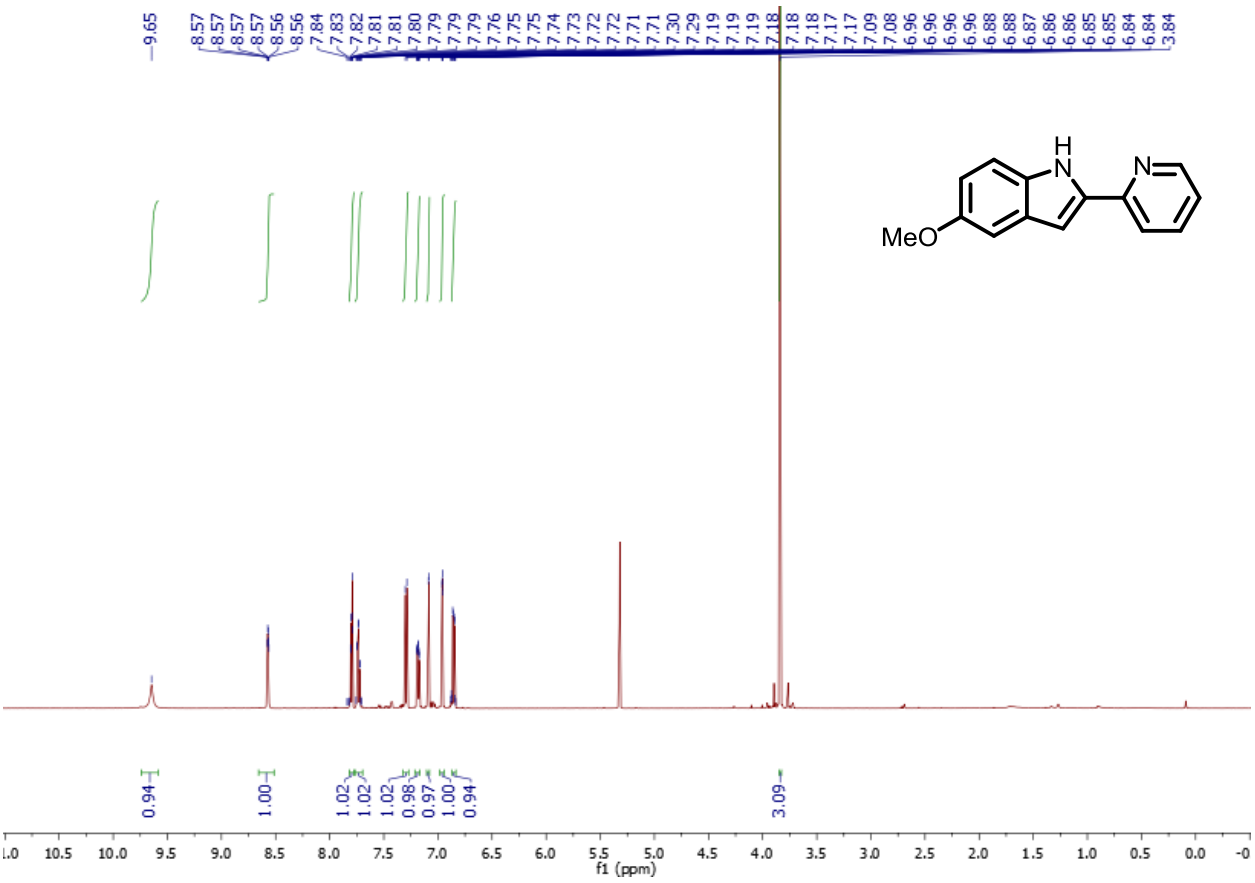


**Figure S53**. $^{13}C\{^{1}H\}$ NMR of **1e** in $CD_2Cl_2$.

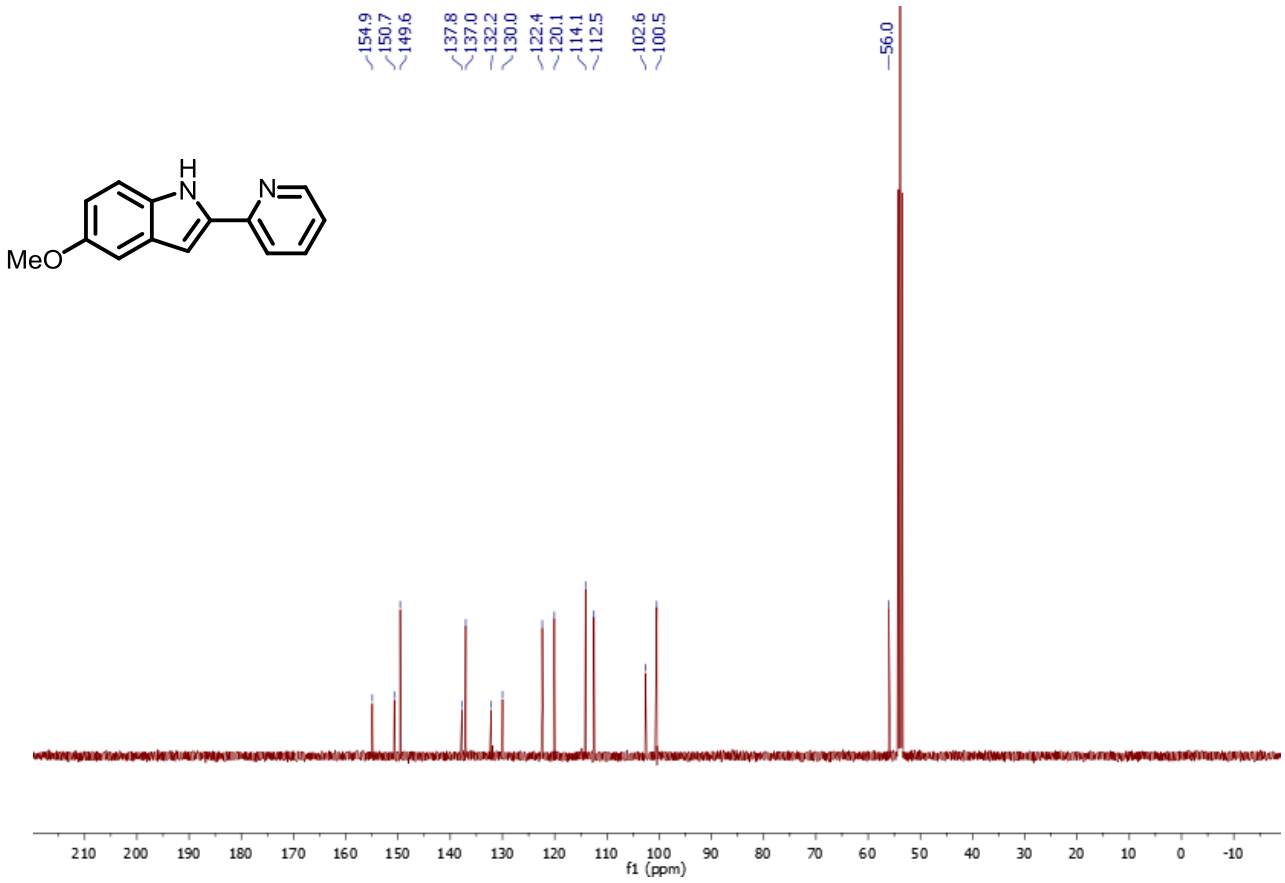


**Figure S54**. $^{1}H$ NMR of **2e** in $CD_2Cl_2$.

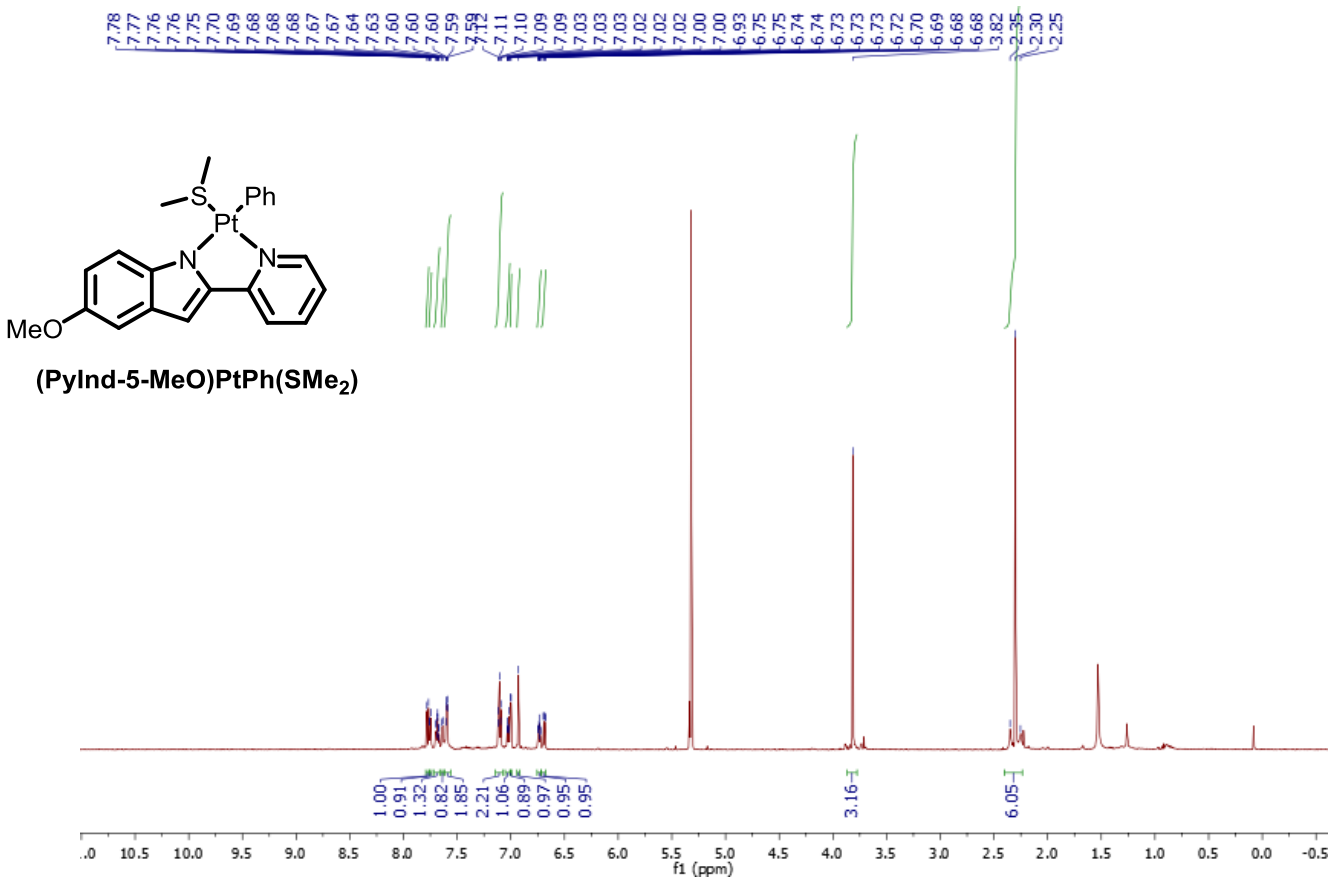


**Figure S55**. $^{13}C\{^{1}H\}$ NMR of **2e** in $CD_2Cl_2$.

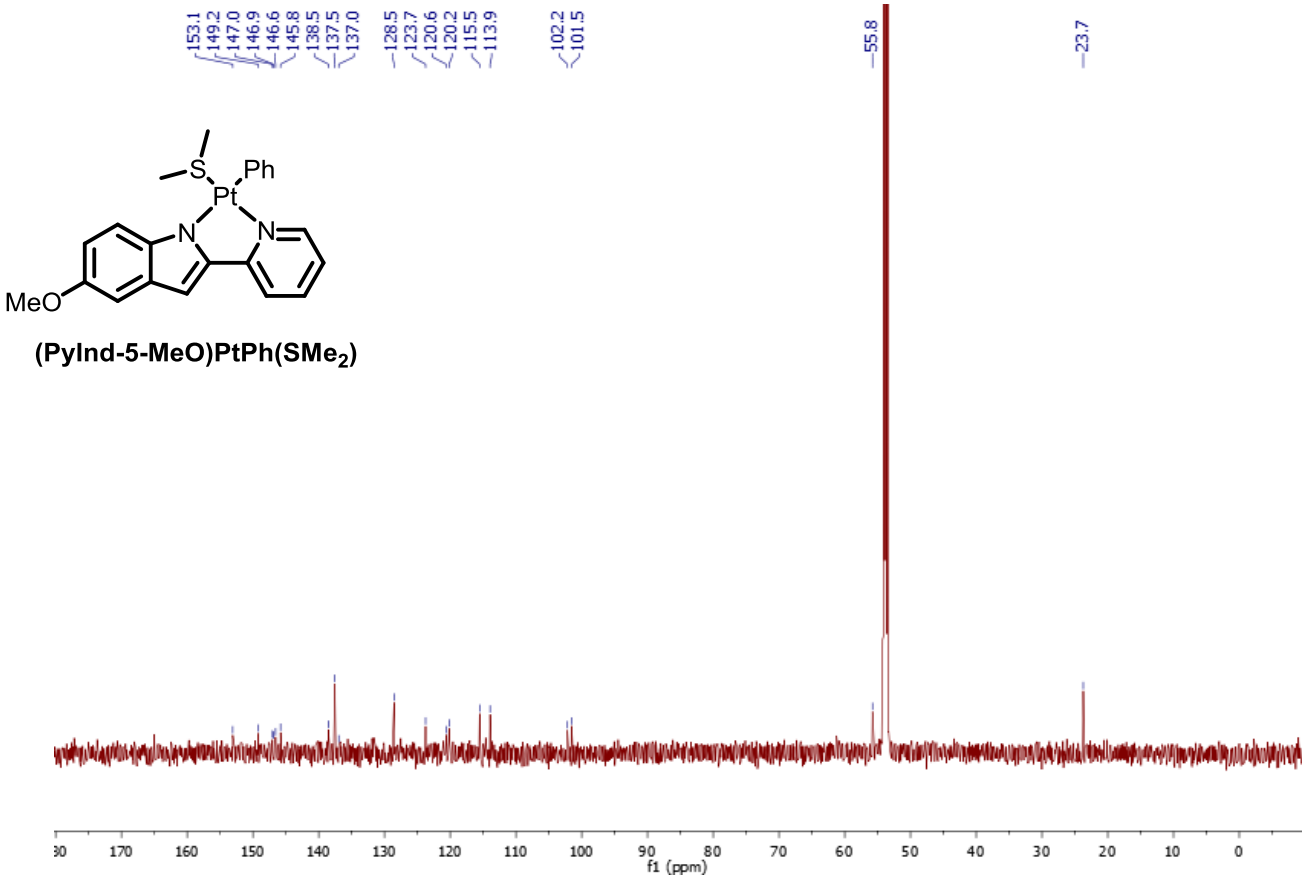


**Figure S56**. $^{1}$H NMR of **S3f** in DMSO-$d_6$.

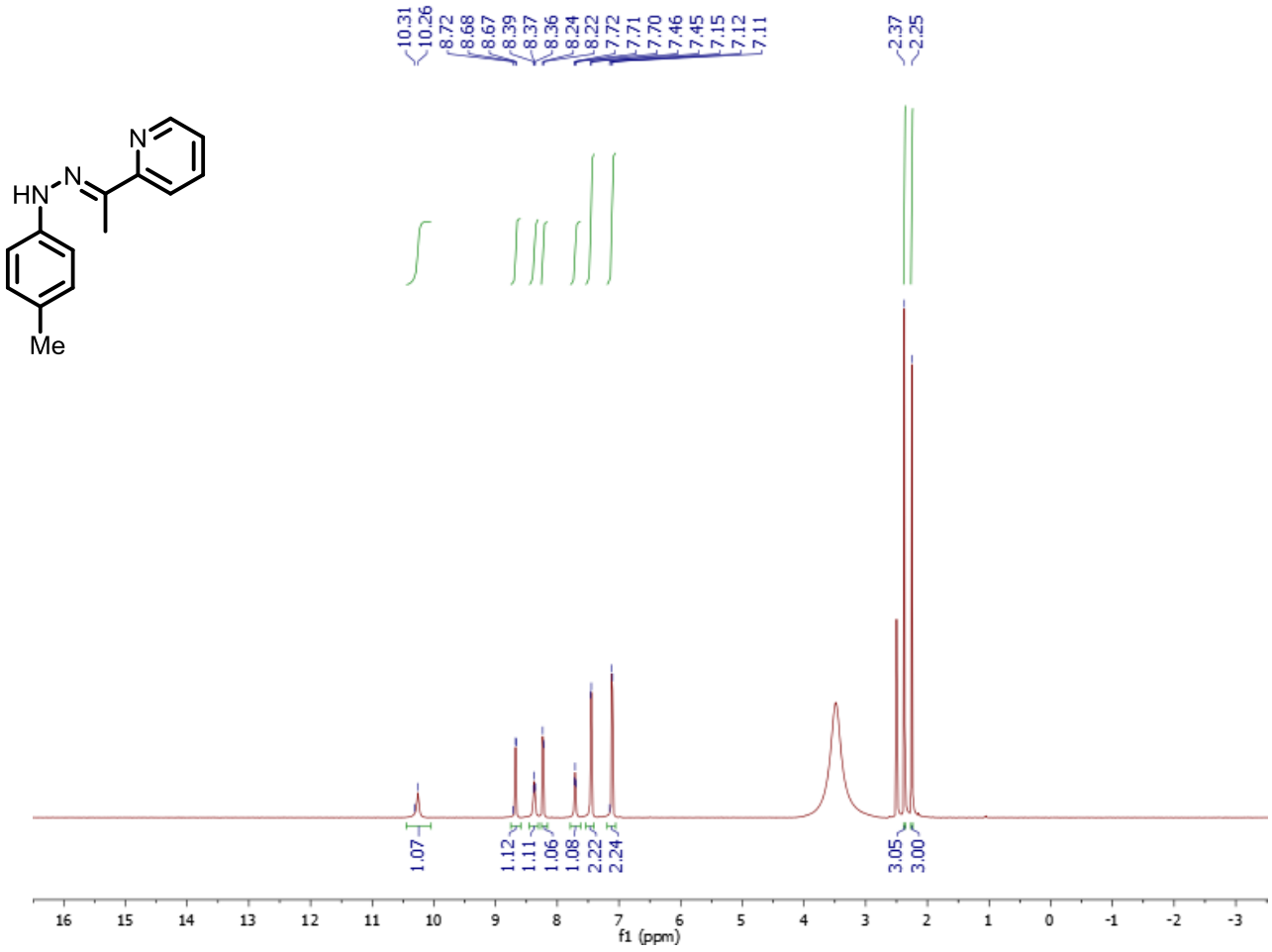


**Figure S57**. $^{13}C\{^{1}H\}$ NMR of **S3f** in DMSO-$d_6$. Insert: expansion from 155.0 ppm to 119.0 ppm.

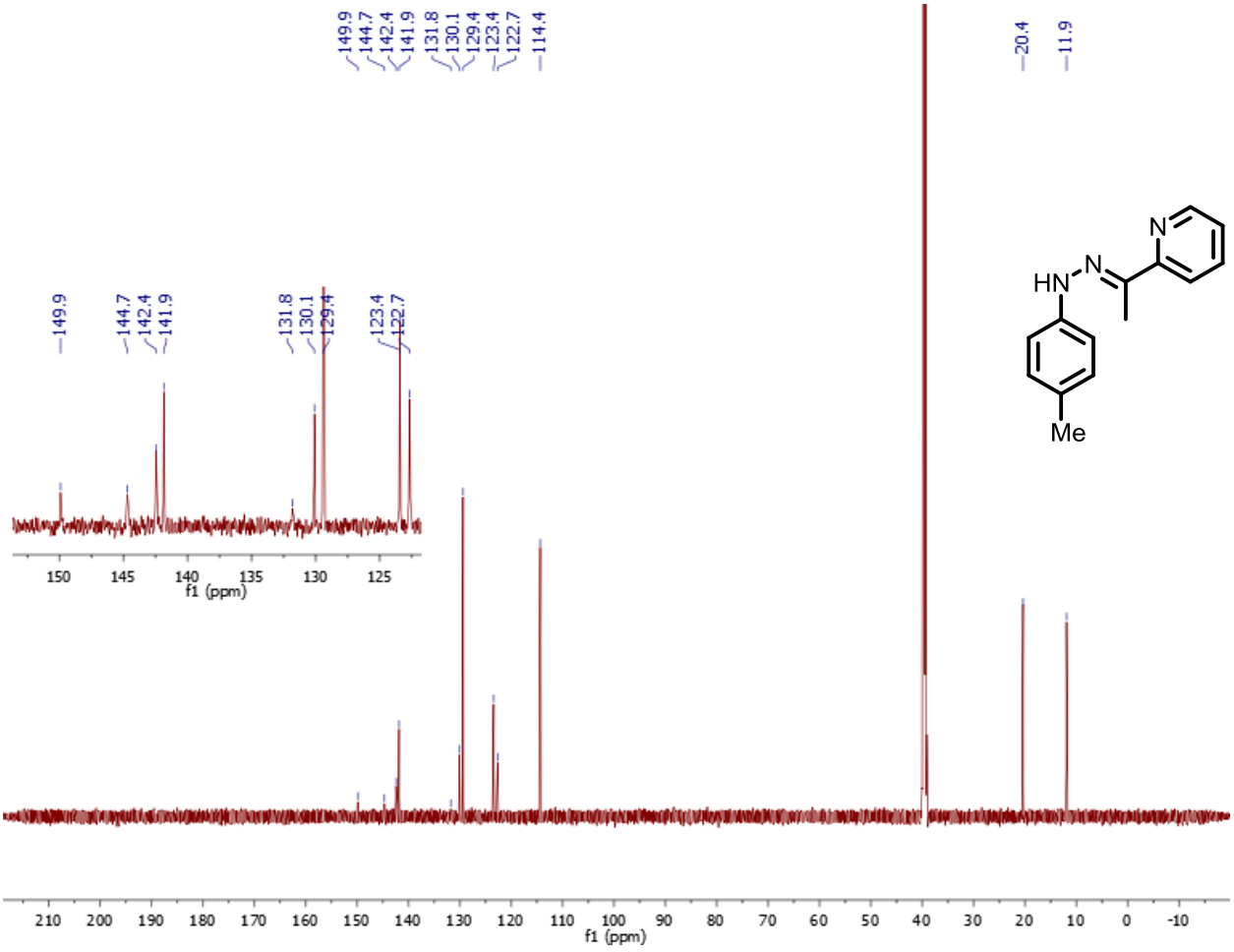


**Figure S58**. $^{1}H$ NMR of **1f** in $CD_2Cl_2$.

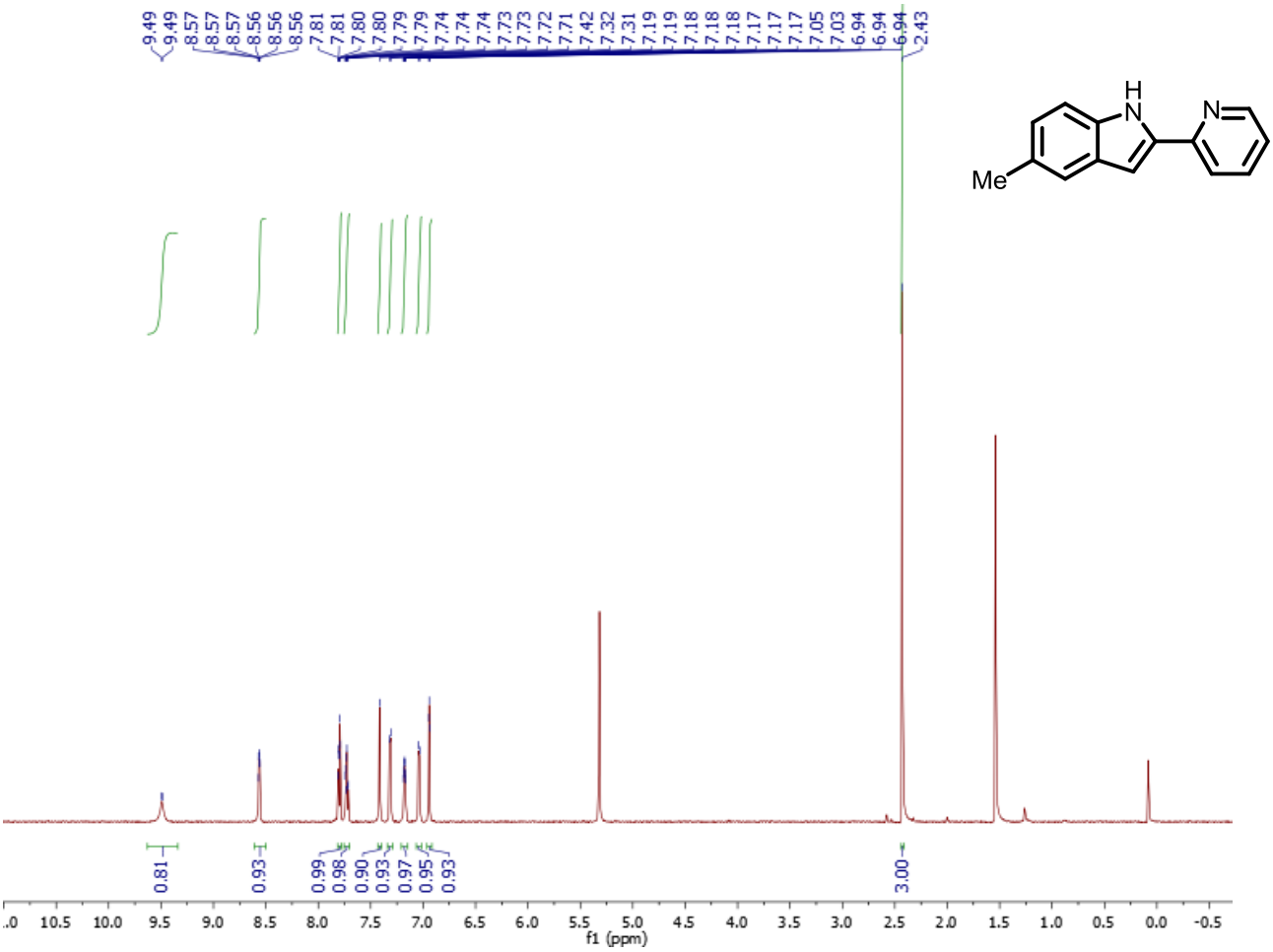


**Figure S59**. $^{13}C\{^{1}H\}$ NMR of **1f** in $CD_2Cl_2$.

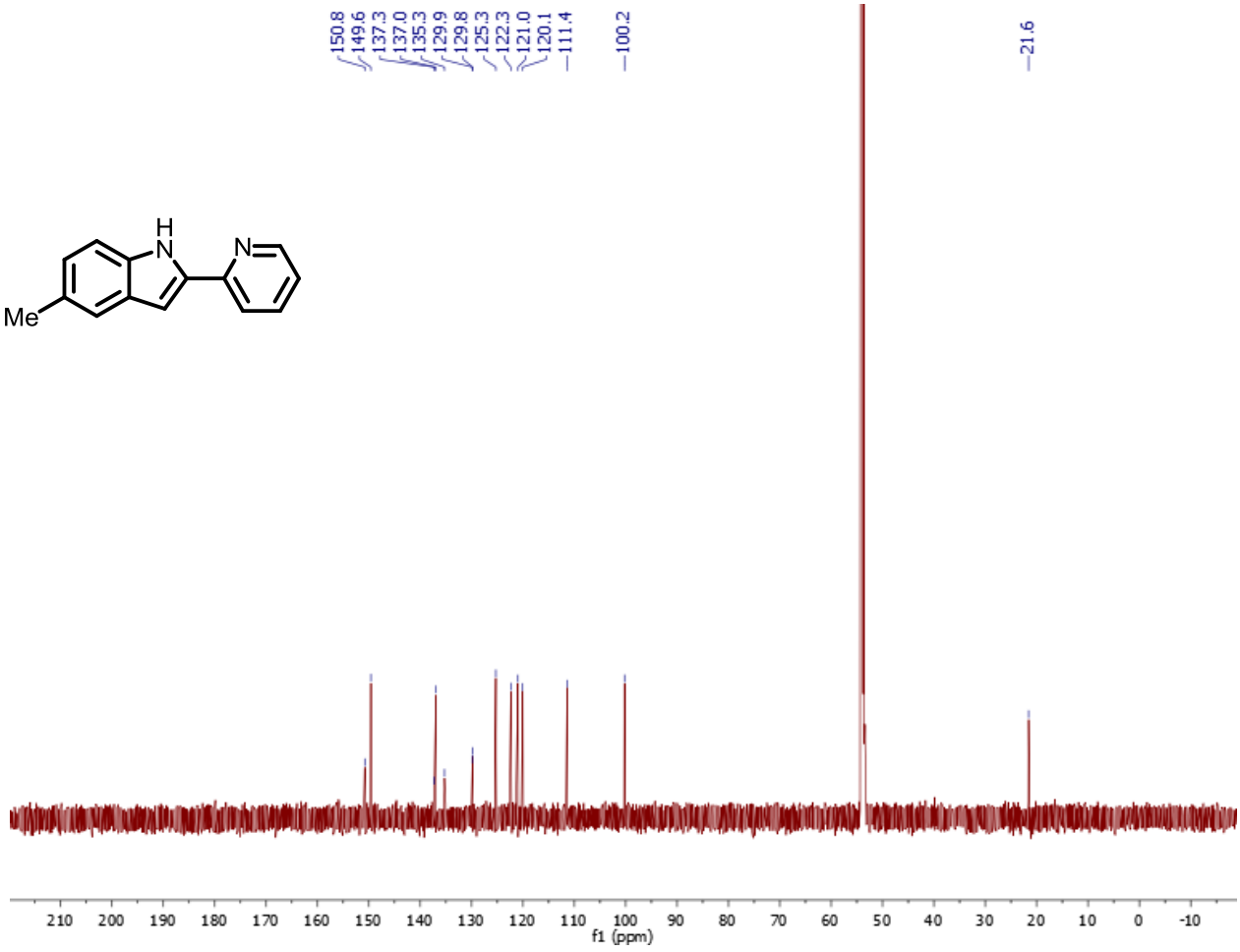


**Figure S60**. $^{1}$H NMR of **2f** in $C_6D_6$.

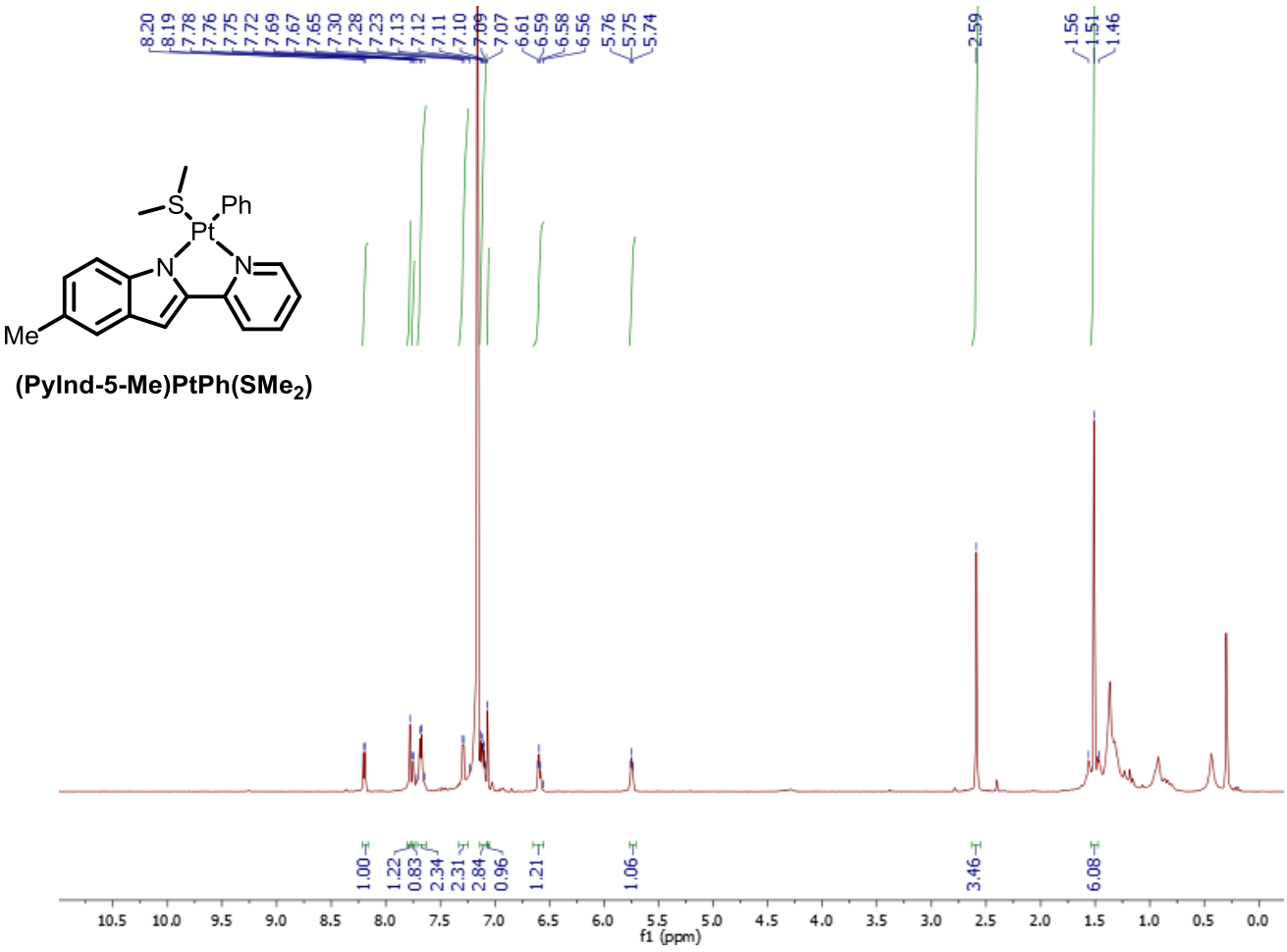


**Figure S61**. $^{13}C\{^{1}H\}$ NMR of **2f** in $C_6D_6$. Insert: expansion from 165.0 to 141.0 ppm.

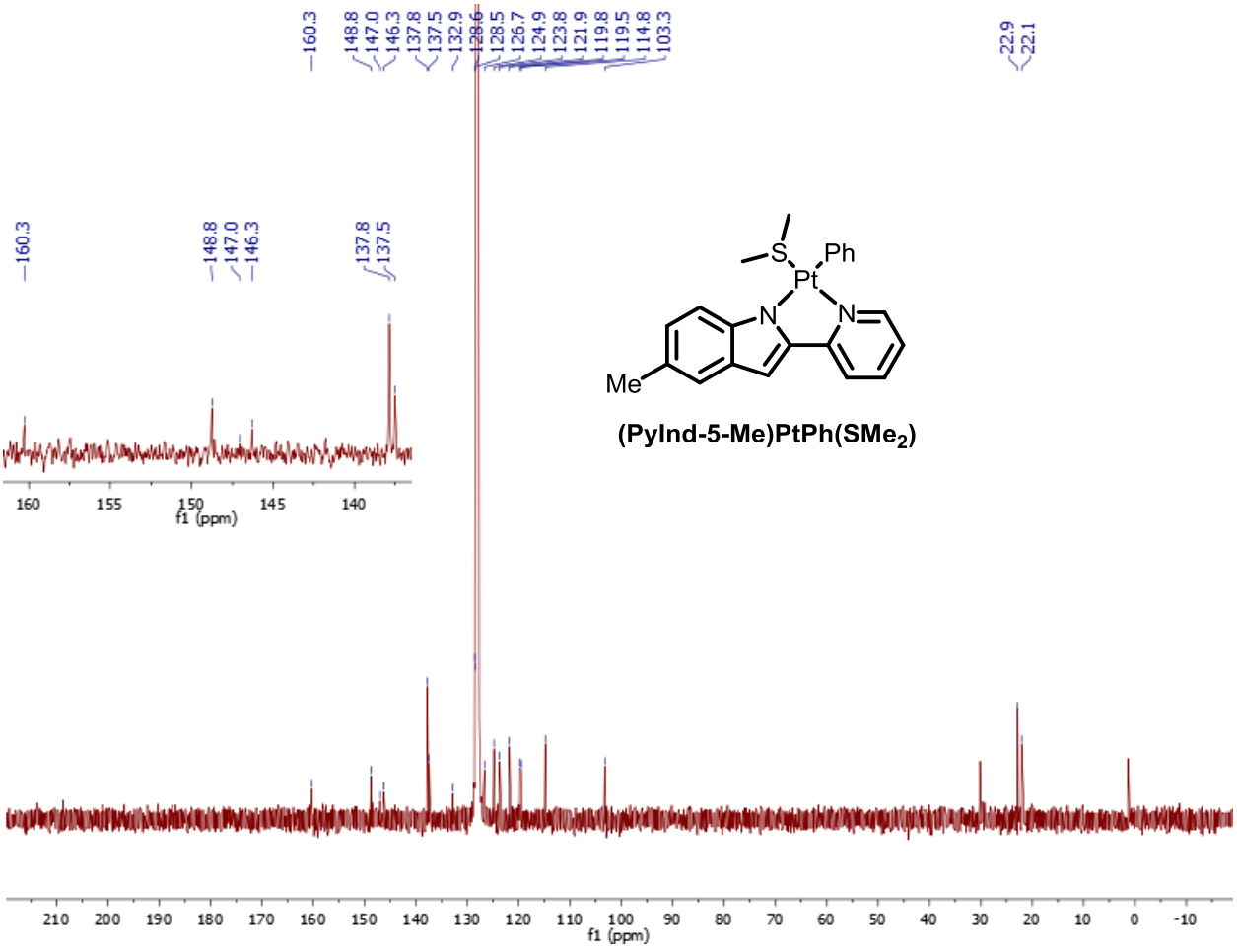


**Figure S62**. $^{1}$H NMR of **S3g** in DMSO-$d_6$.

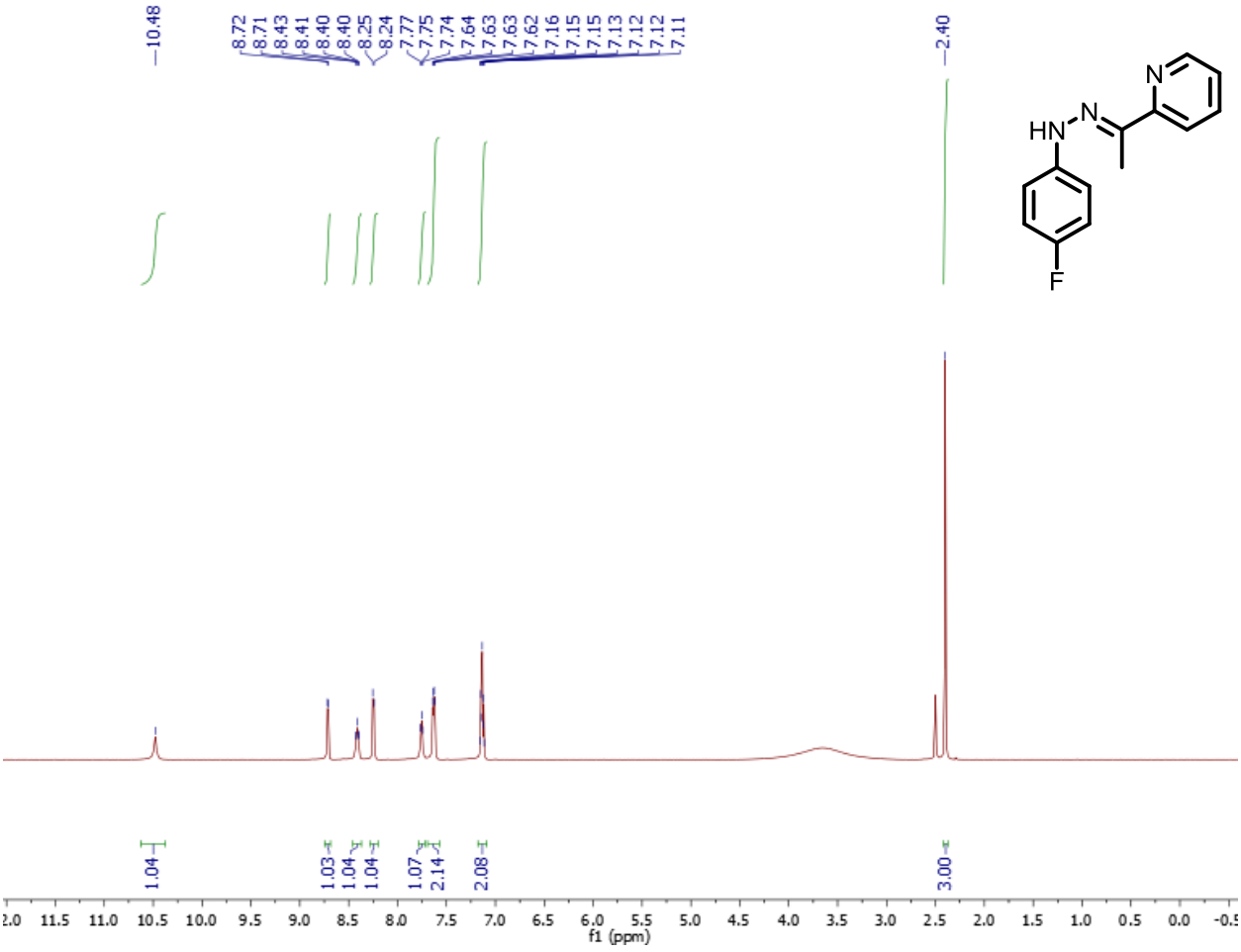


**Figure S63**. $^{13}C\{^{1}H\}$ NMR of **S3g** in DMSO-$d_6$. Insert: expansion from 160.0 to 130.0 ppm.

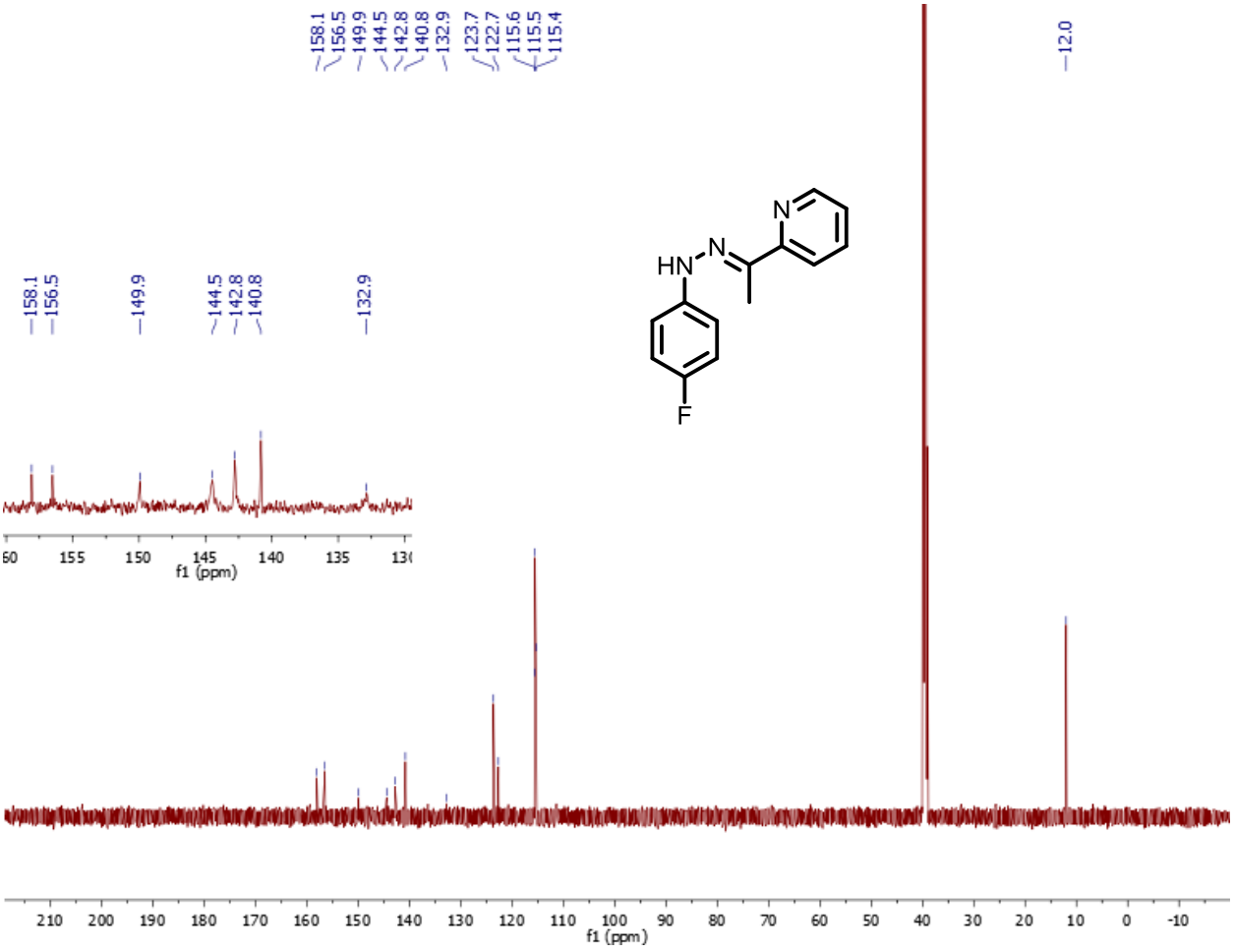


**Figure S64**. $^{19}F$ NMR of **S3g** in DMSO-$d_6$. Insert: expansion of $^{19}F$ resonance centered at -122.5 ppm.

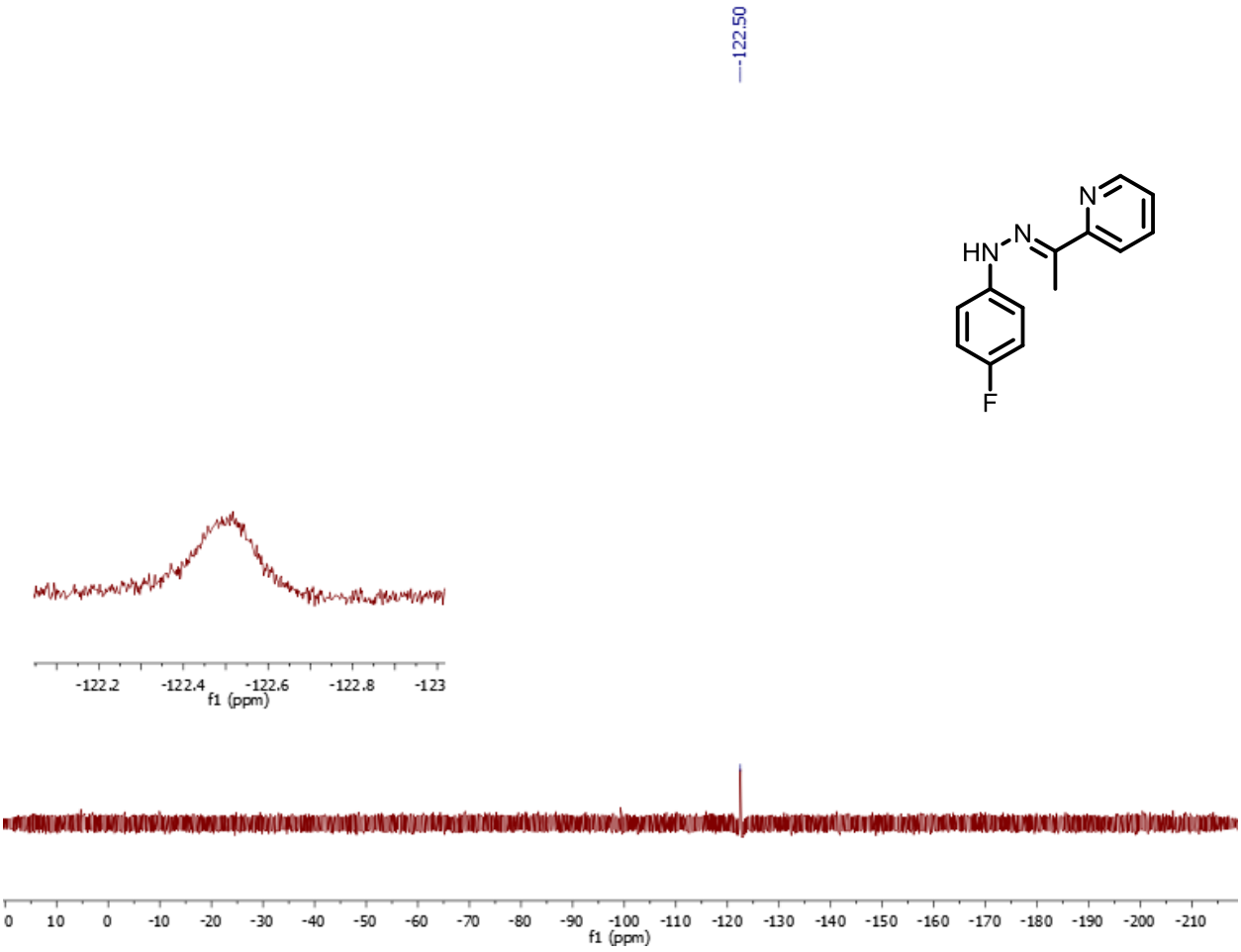


**Figure S65**. $^{1}H$ NMR of **1g** in $CD_2Cl_2$.

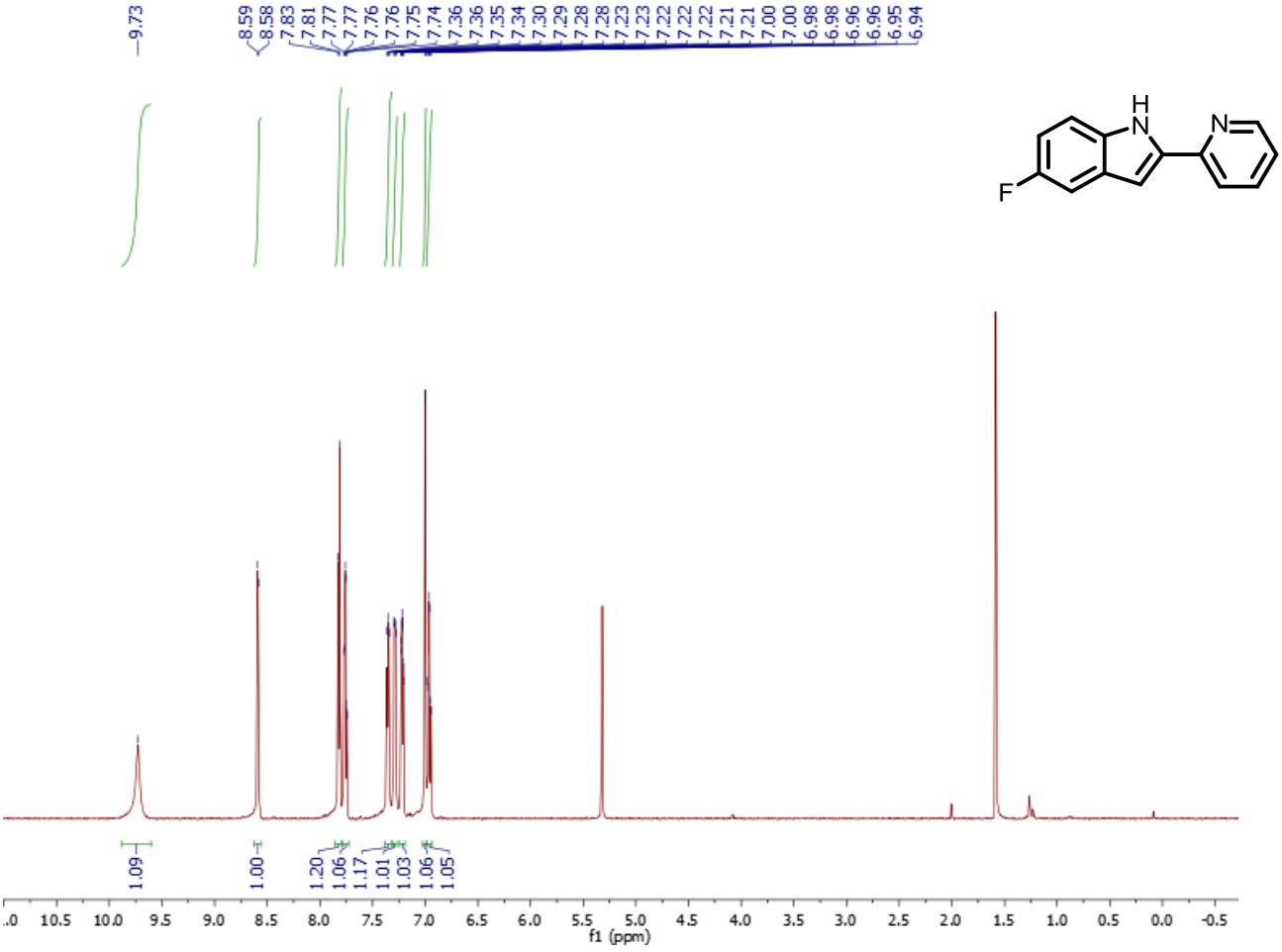


**Figure S66**. $^{13}C\{^{1}H\}$ NMR of **1g** in $CD_2Cl_2$.

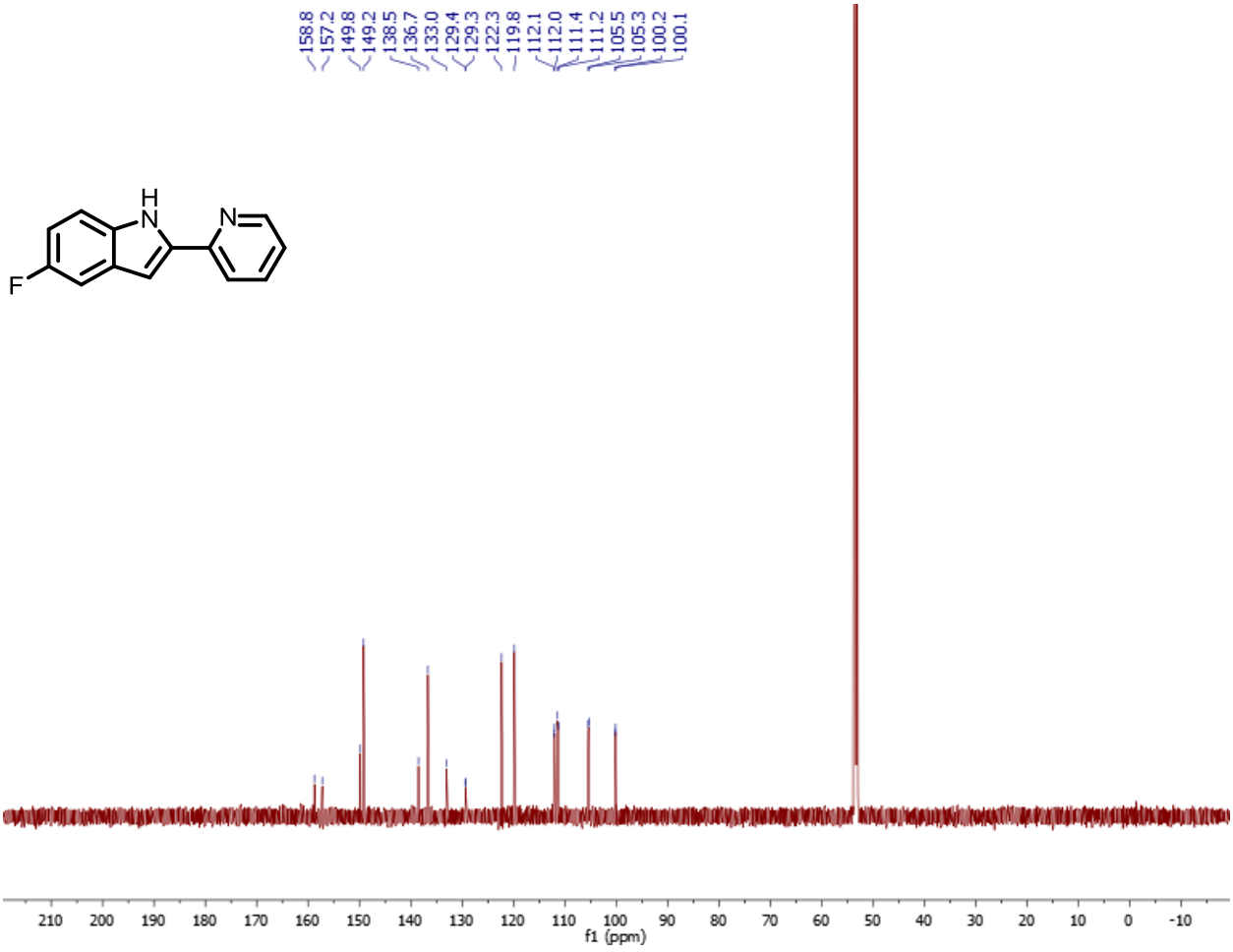


**Figure S67**. $^{19}F$ NMR of **1g** in $CD_2Cl_2$. Insert: expansion of $^{19}F$ resonance centered at -124.2 ppm.

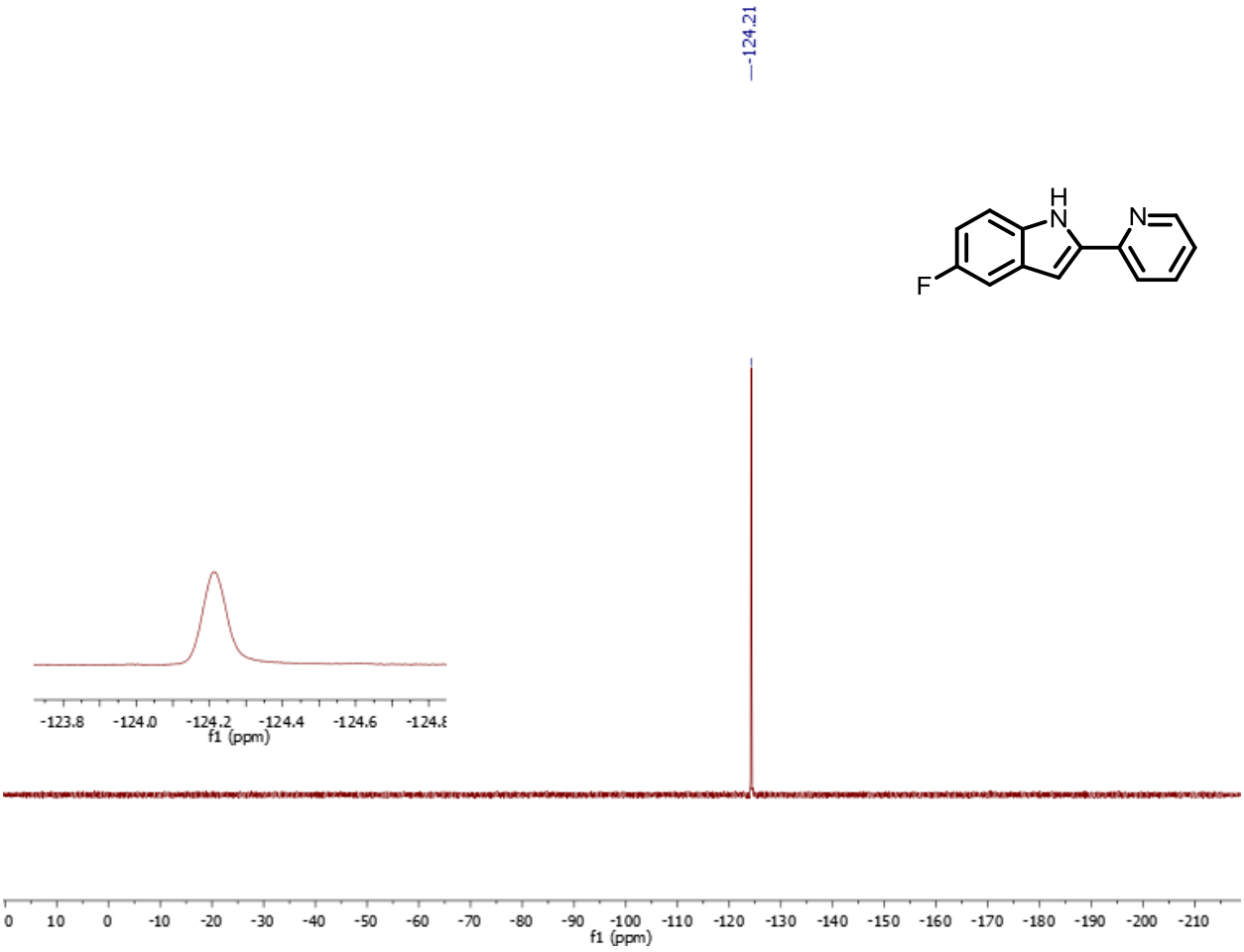


**Figure S68**. $^{1}H$ NMR of **2g** in $CD_2Cl_2$.

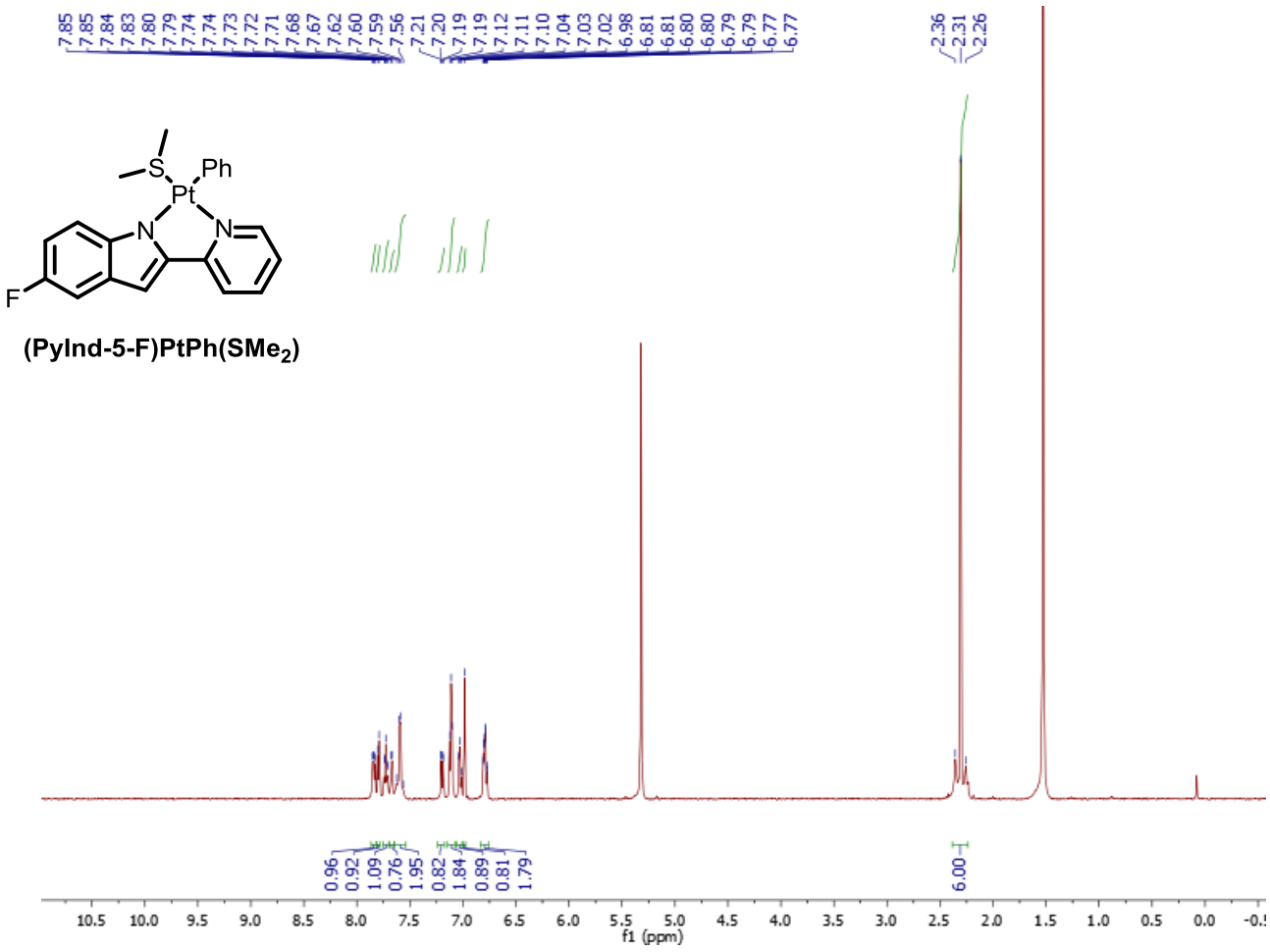


**Figure S69**. $^{13}C\{^{1}H\}$ NMR of **2g** in $CD_2Cl_2$. Insert: expansion from 165.0 to 140.0 ppm.

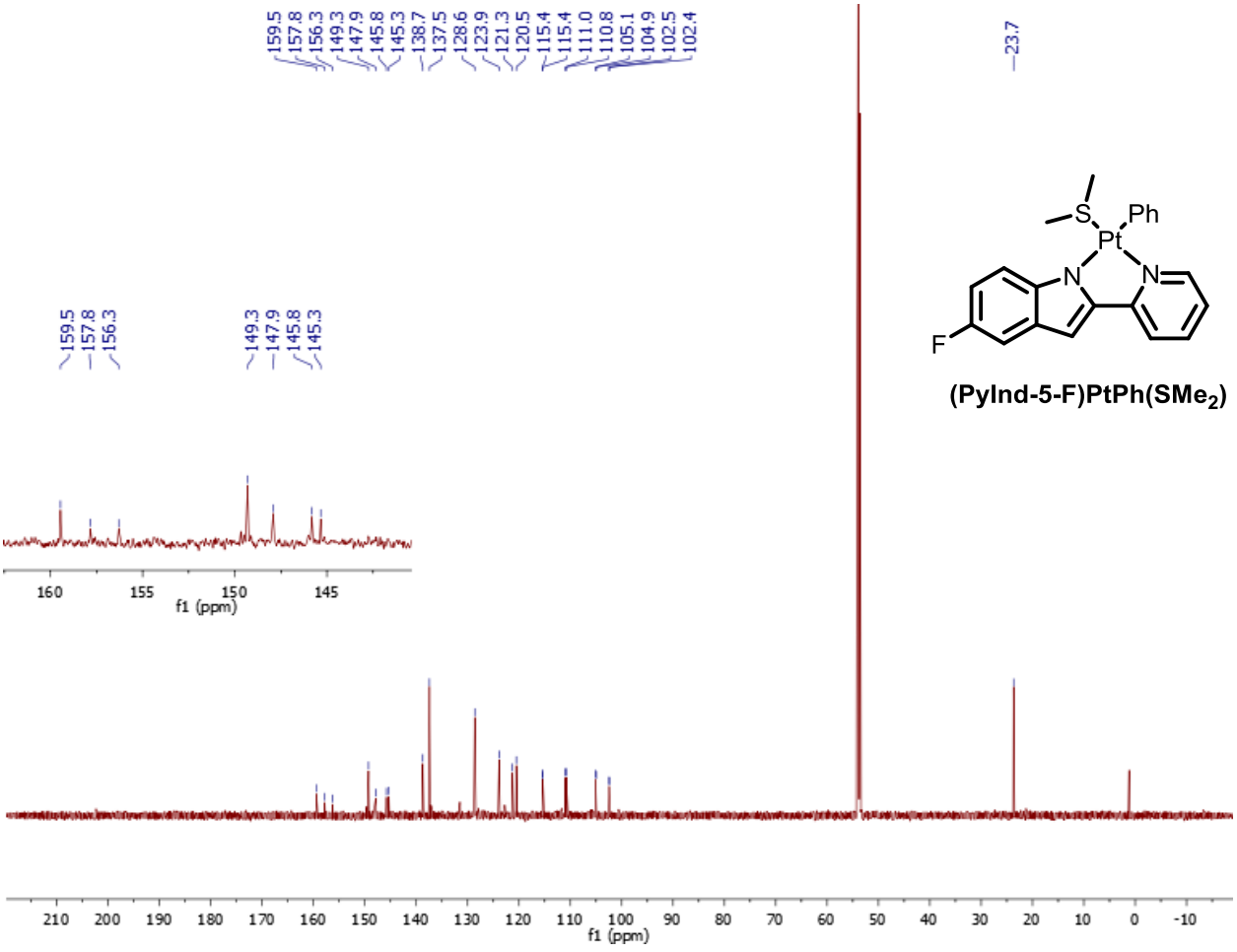


**Figure S70**. $^{19}F$ NMR of **2g** in $CD_2Cl_2$. Insert: expansion of $^{19}F$ resonance centered at -127.0 ppm.

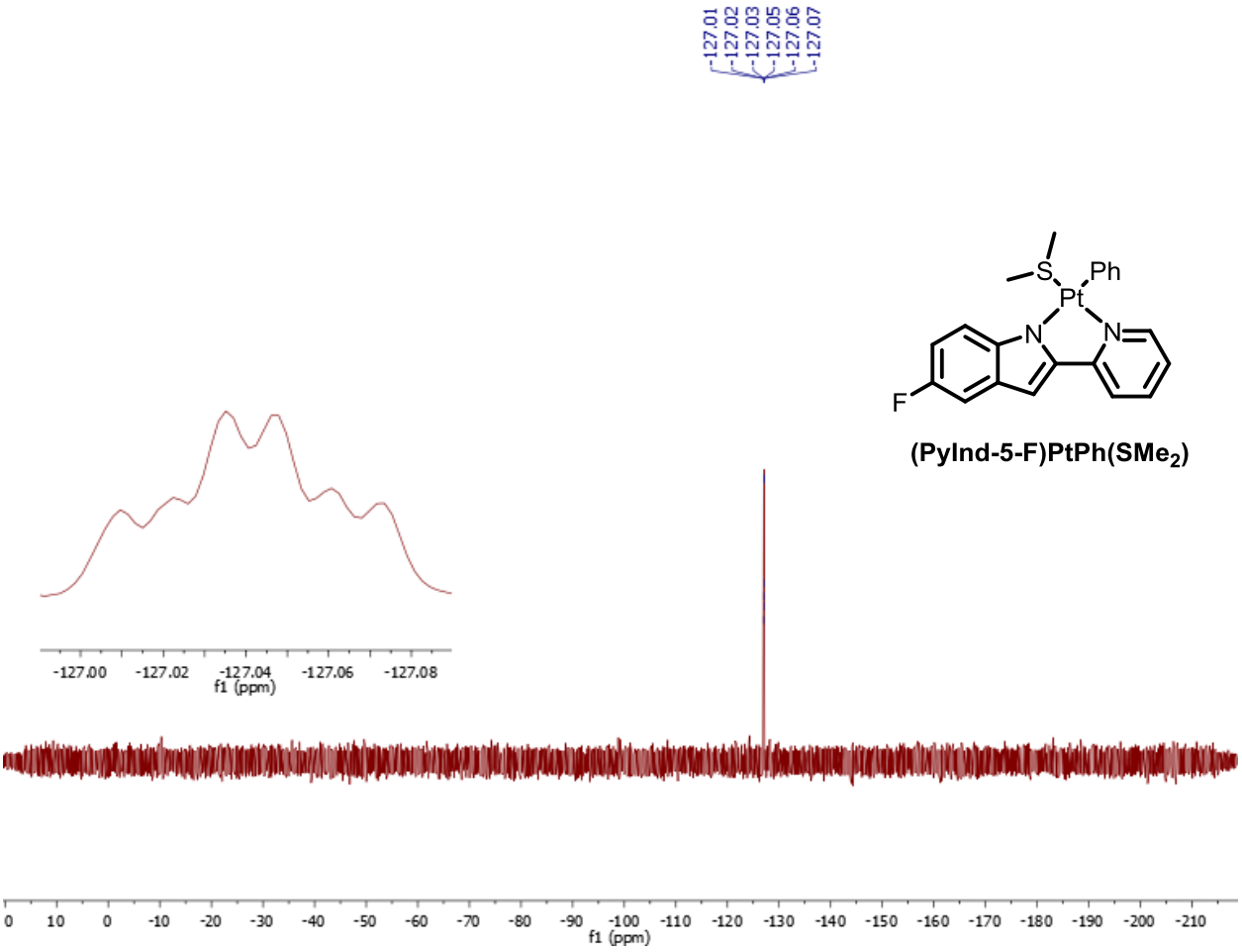


**Figure S71**. $^{1}$H NMR of **S3h** in DMSO-$d_6$.

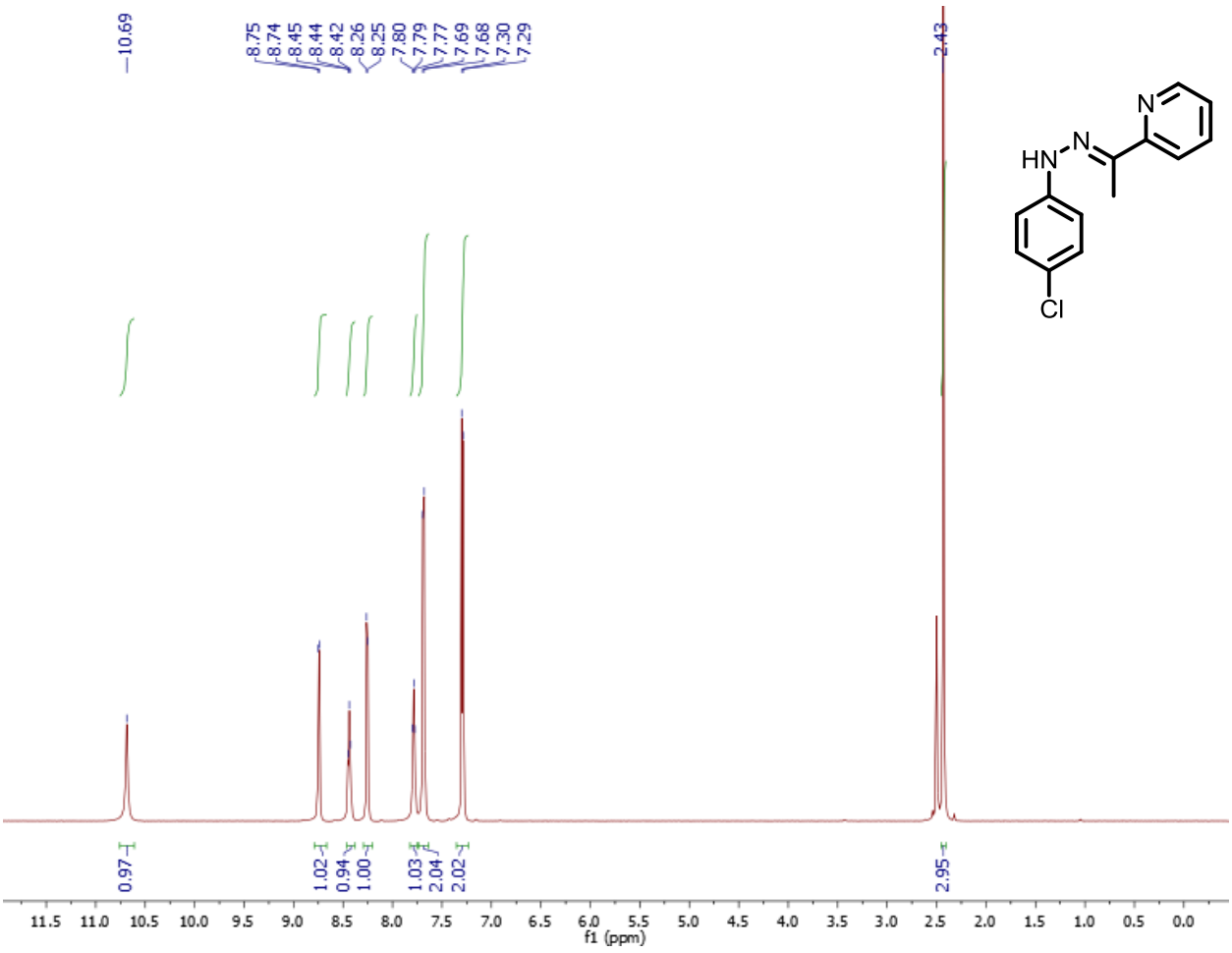


**Figure S72**. $^{13}C\{^{1}H\}$ NMR of **S3h** in DMSO-$d_6$. Insert: expansion form 150.0 to 133.0 ppm.

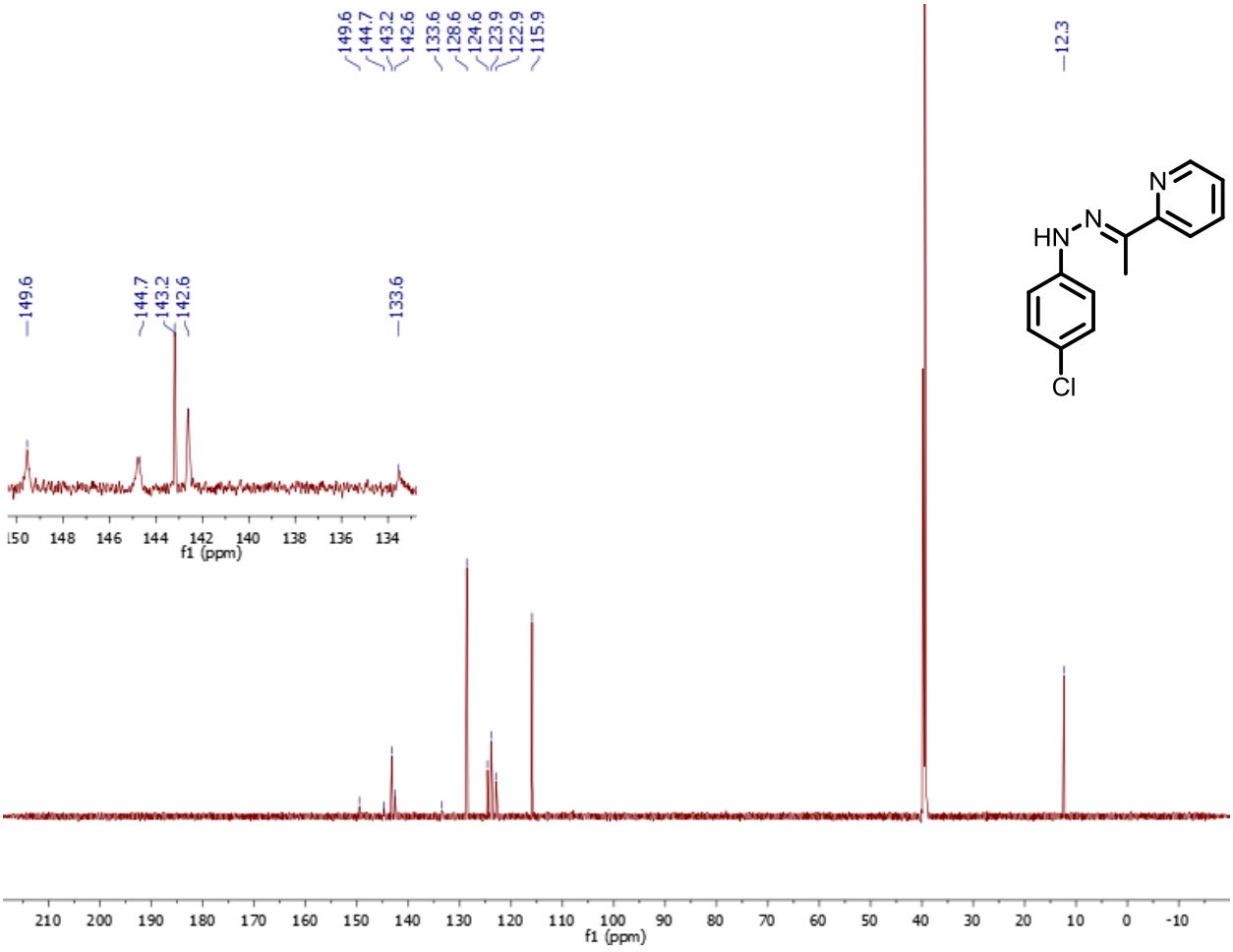


**Figure S73**. $^{1}H$ NMR of **1h** in $CD_2Cl_2$.

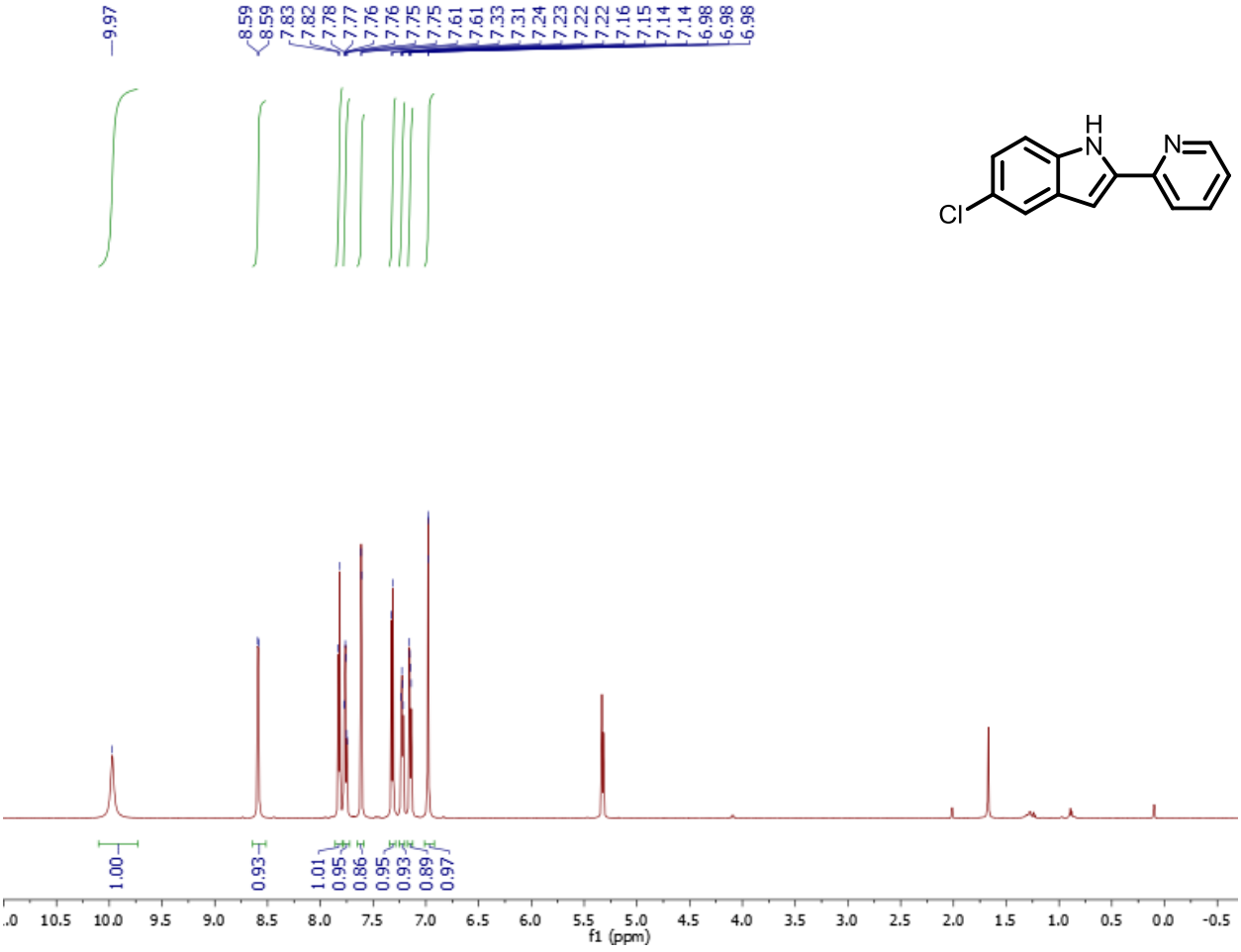


**Figure S74**. $^{13}C\{^{1}H\}$ NMR of **1h** in $CD_2Cl_2$.

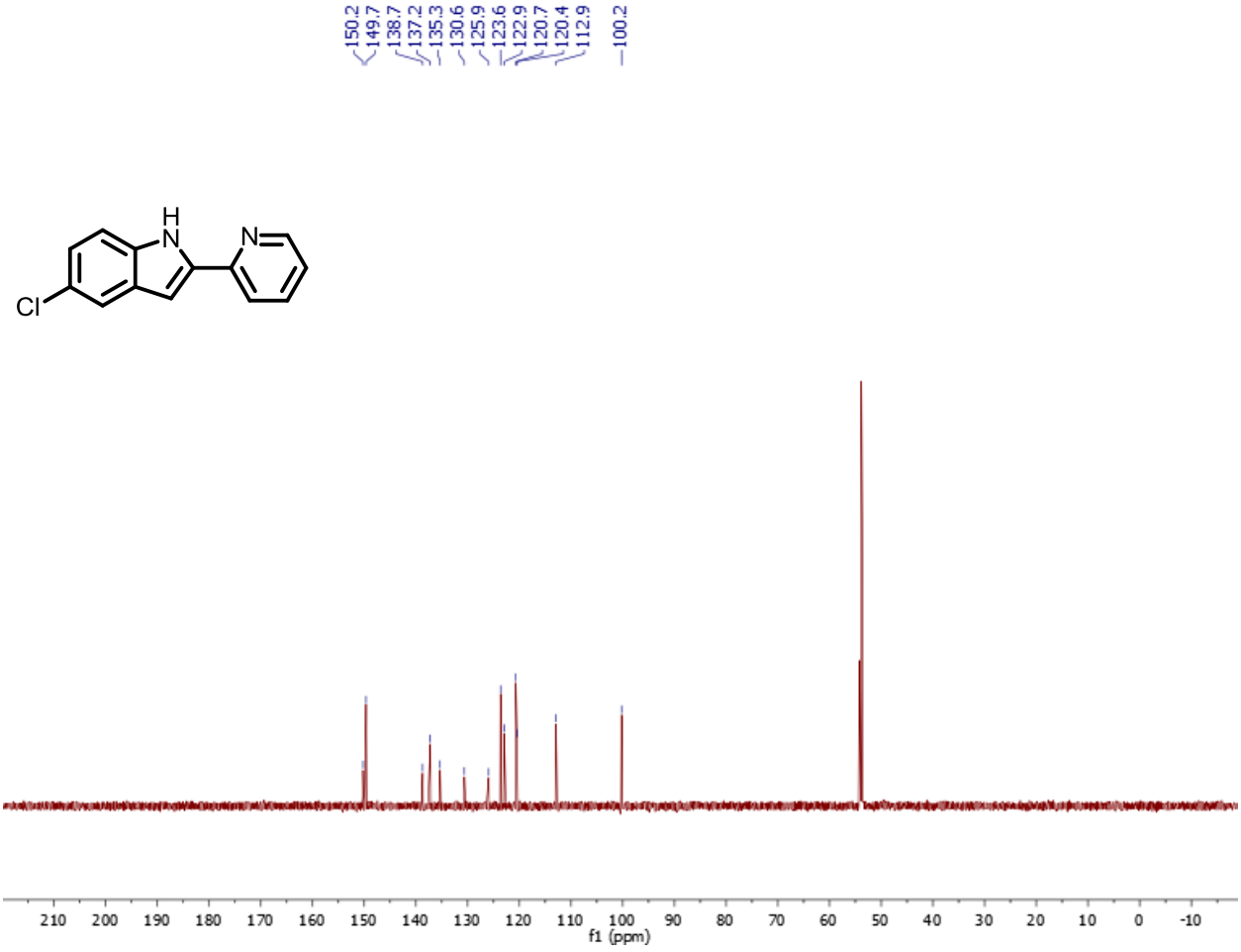


**Figure S75**. $^{1}$H NMR of **2h** in $CD_2Cl_2$.

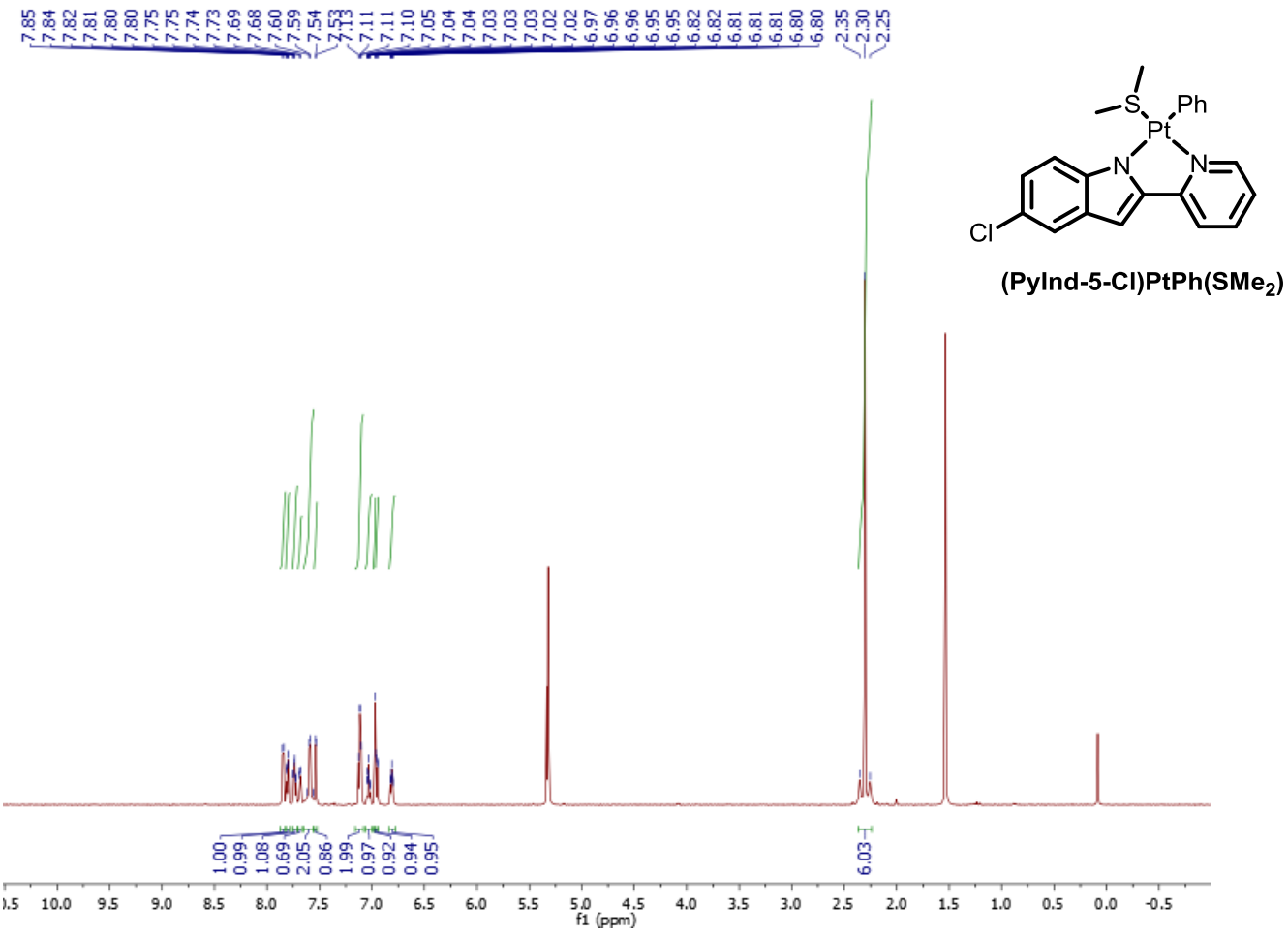


**Figure S76**. $^{13}C\{^{1}H\}$ NMR of **2h** in $CD_2Cl_2$. Insert: expansion from 160.0 to 145.0 ppm.

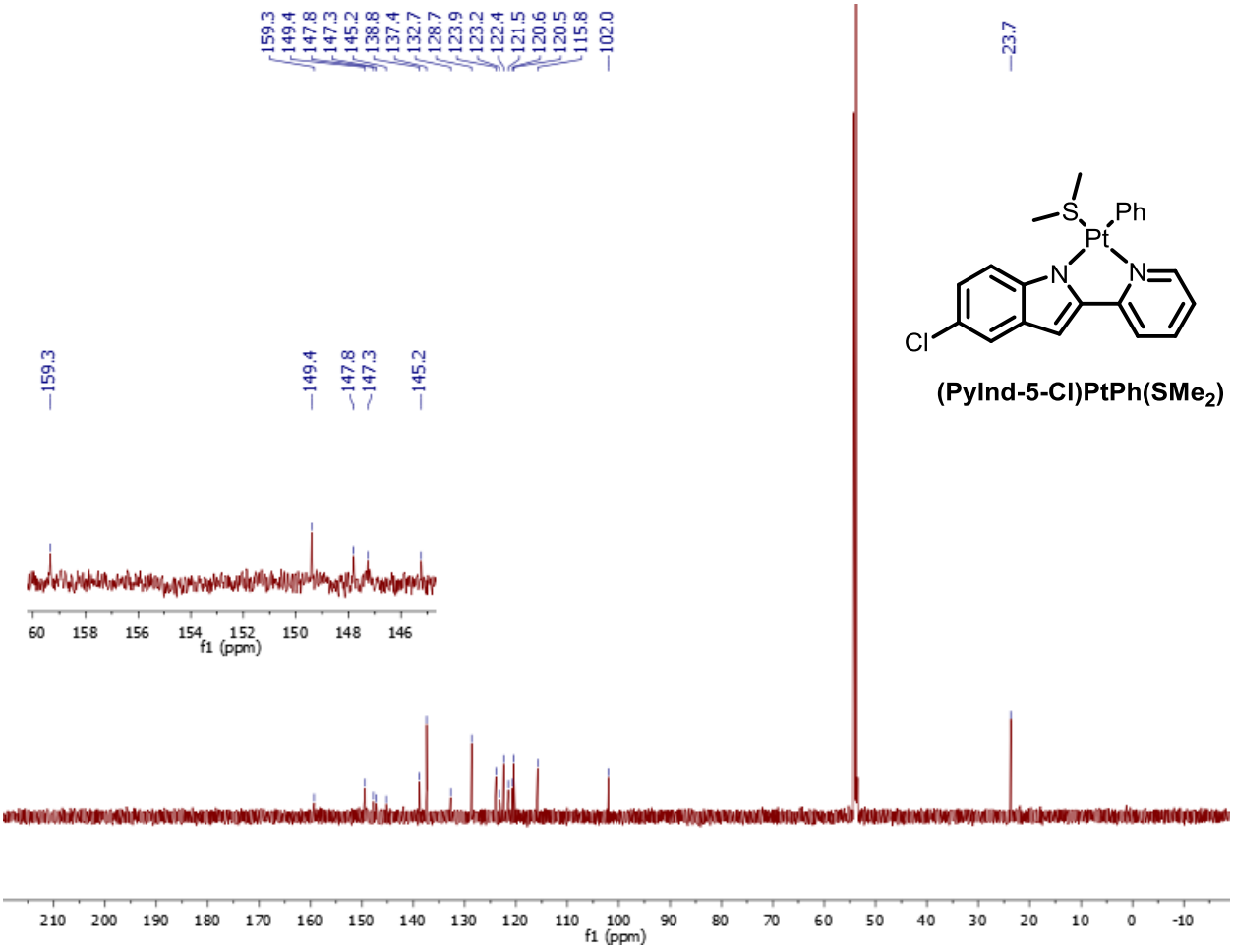


**Figure S77**. $^{1}$H NMR of **S3i** in DMSO-$d_6$.

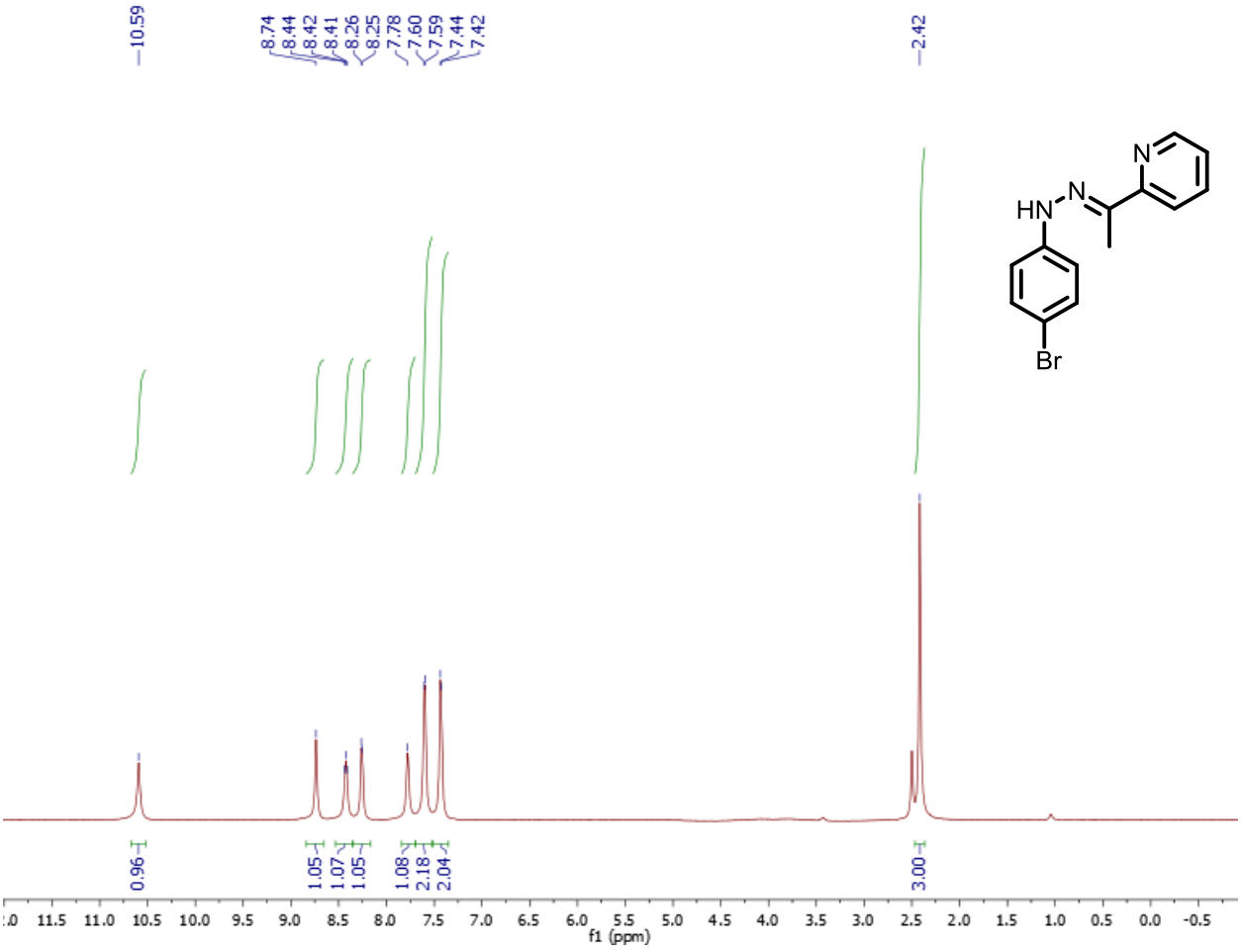


**Figure S78**. $^{13}C\{^{1}H\}$ NMR of **S3i** in DMSO-$d_6$. Insert: expansion from 150.0 to 141.0 ppm.

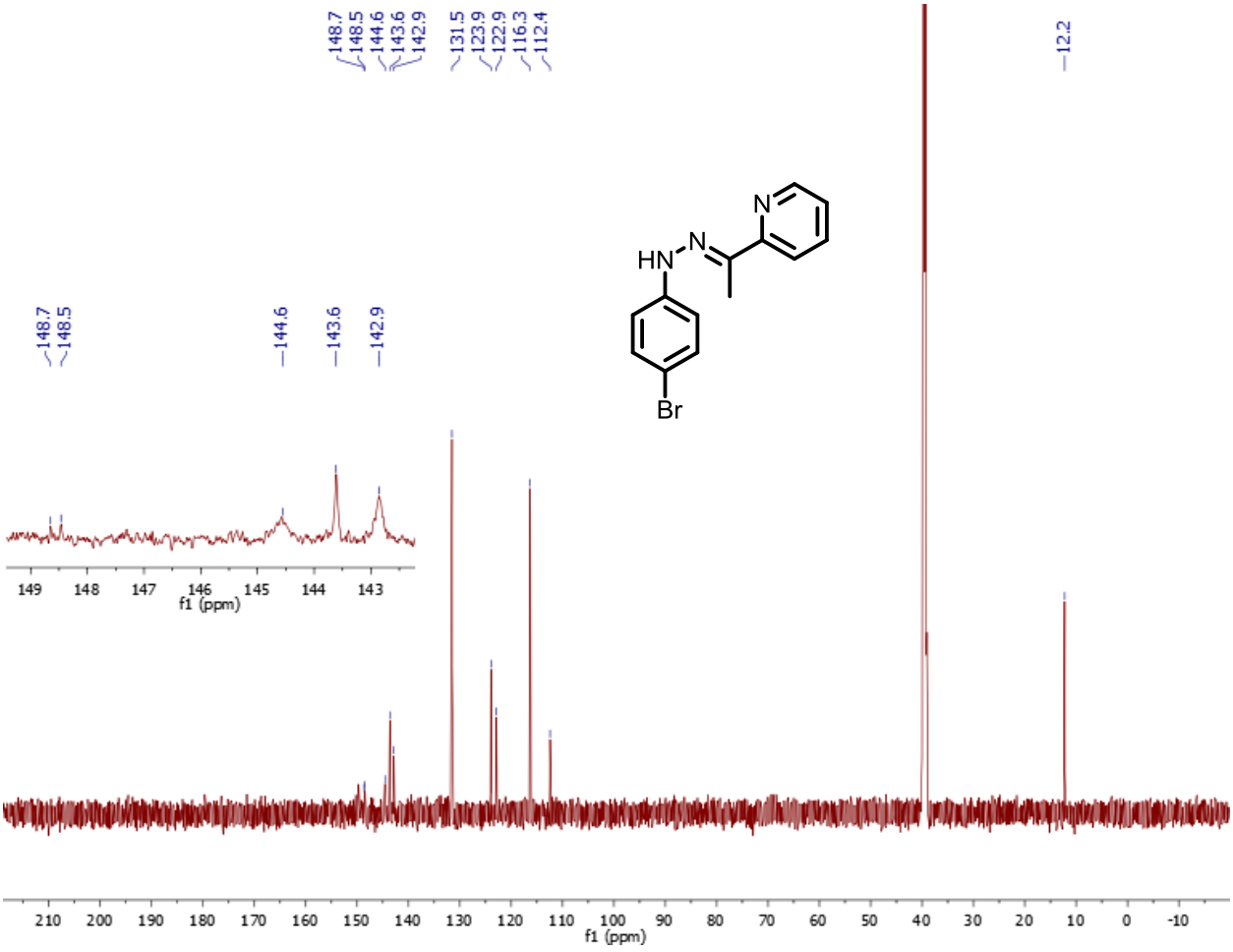


**Figure S79**. $^{1}H$ NMR of **1i** in $C_6D_6$.

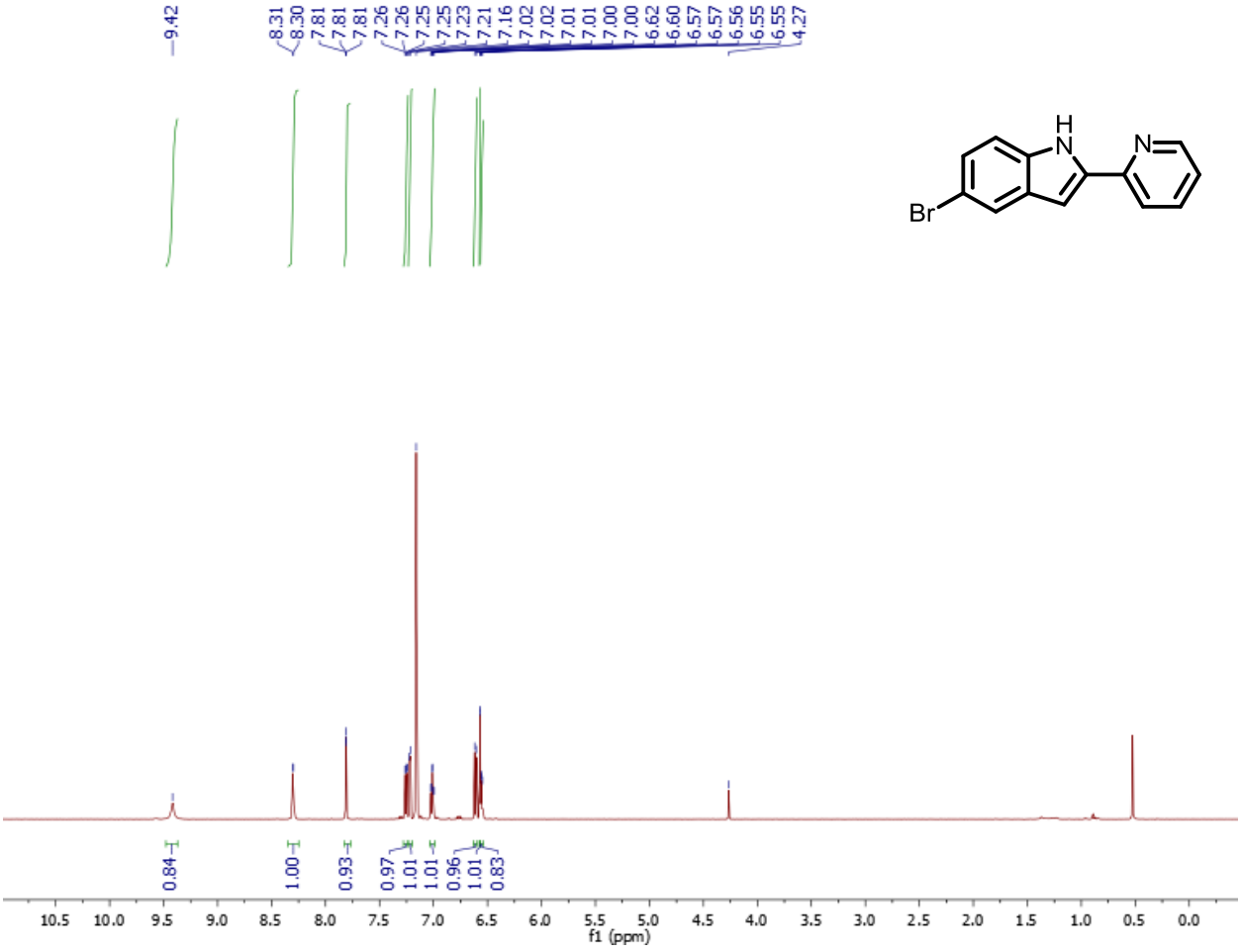


**Figure S80**. $^{13}C\{^{1}H\}$ NMR of **1i** in $C_6D_6$.

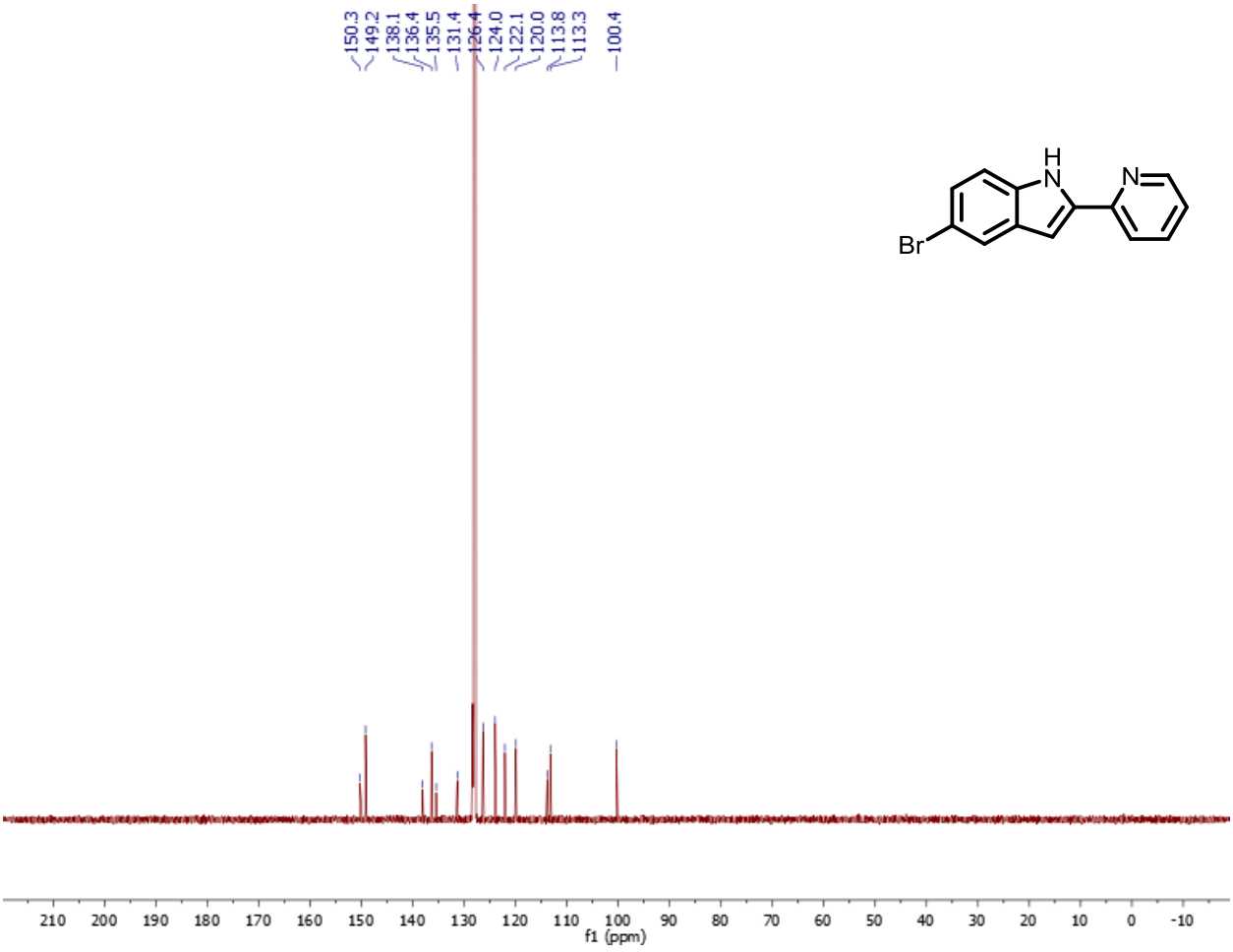


**Figure S81**. $^{1}H$ NMR of **2i** in $CD_2Cl_2$.

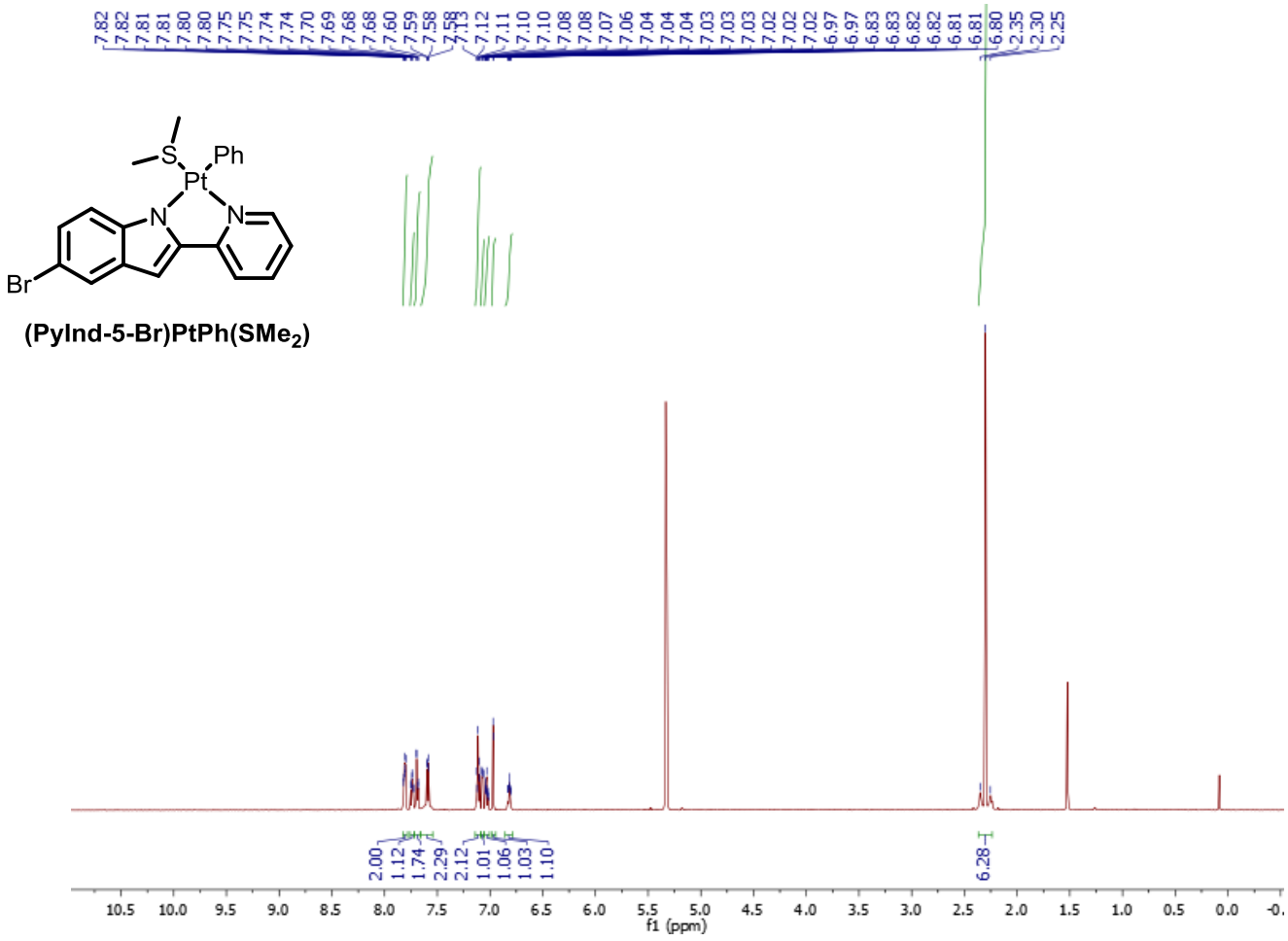


**Figure S82**. $^{13}C\{^{1}H\}$ NMR of **2i** in $CD_2Cl_2$. Insert: expansion from 163.0 to 130.0 ppm.

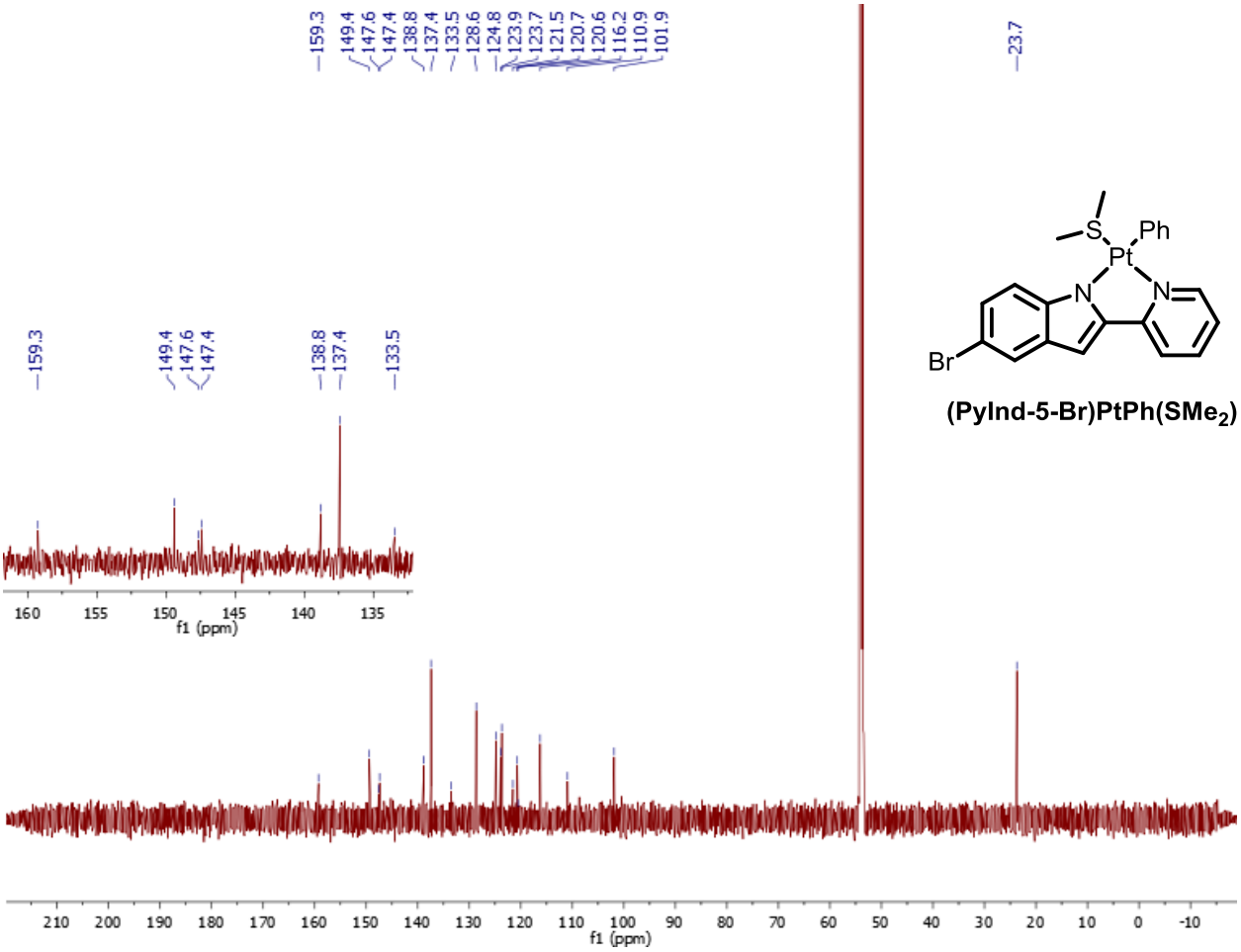


**Figure S83**. $^{1}$H NMR of **S3j** in DMSO-$d_6$.

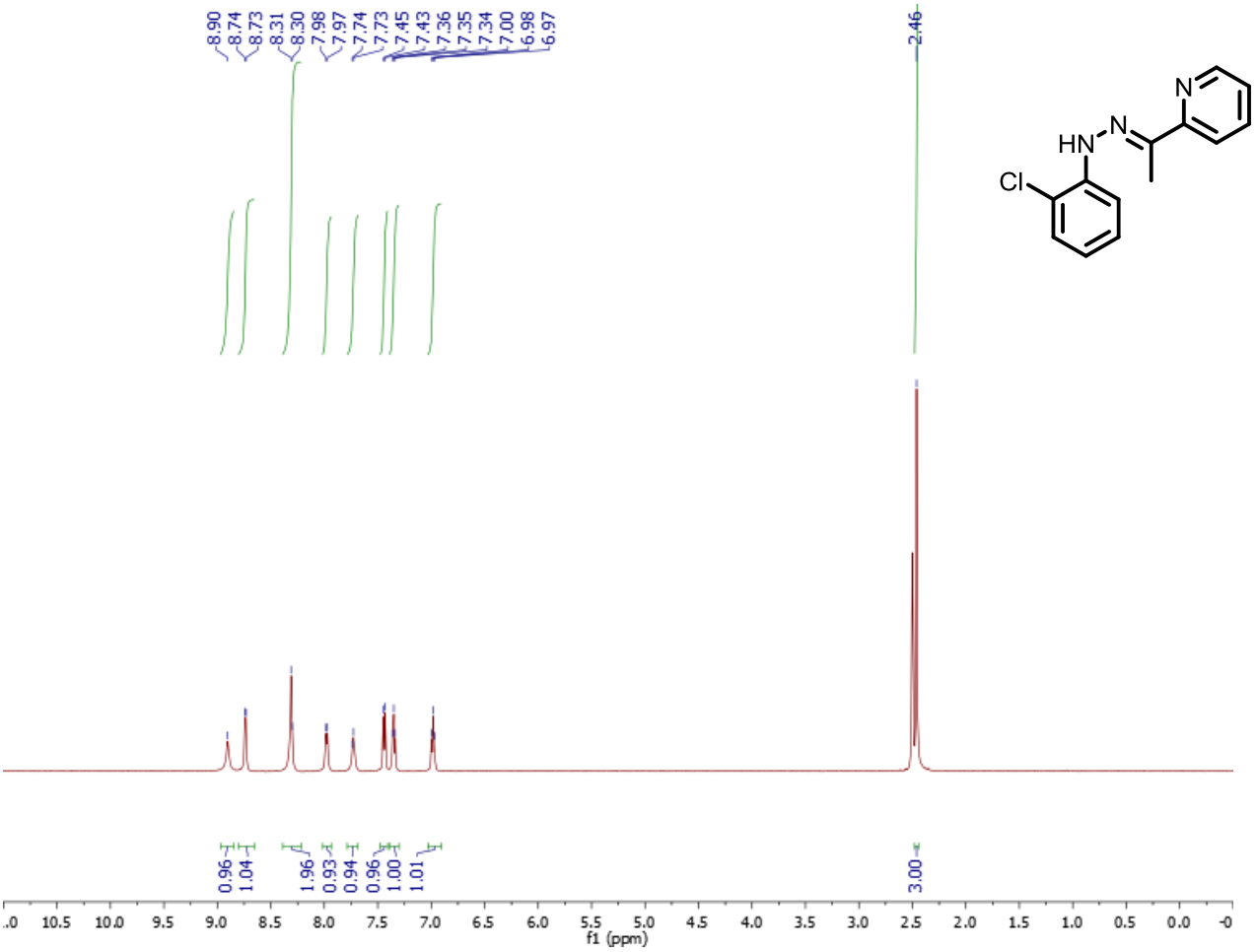


**Figure S84**. $^{13}C\{^{1}H\}$ NMR of **S3j** in DMSO-$d_6$. Insert: expansion from 145.0 to 138.0 ppm and 130.0 to 113.0 ppm.

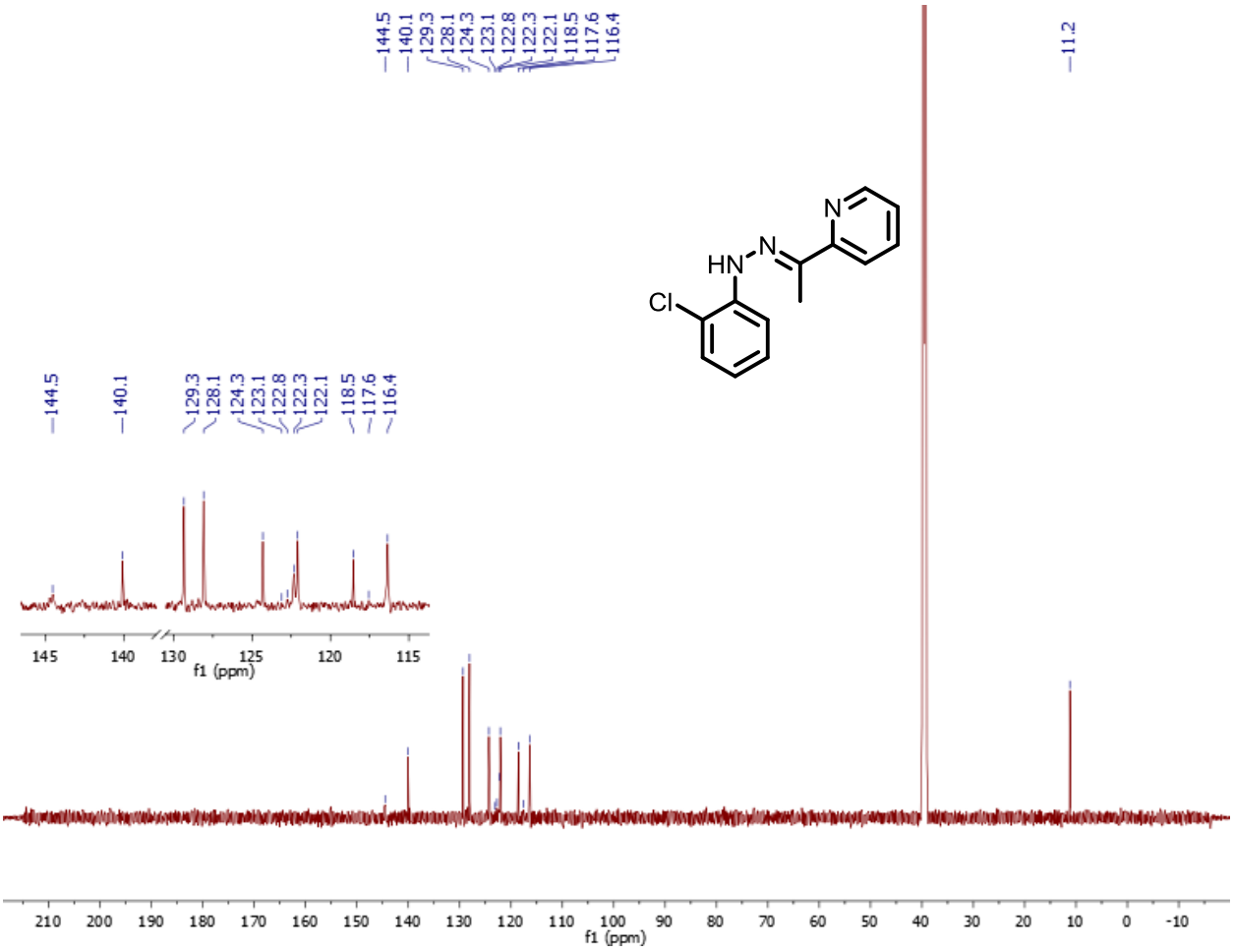


**Figure S85**. $^{1}H$ NMR of **1j** in $CD_2Cl_2$.

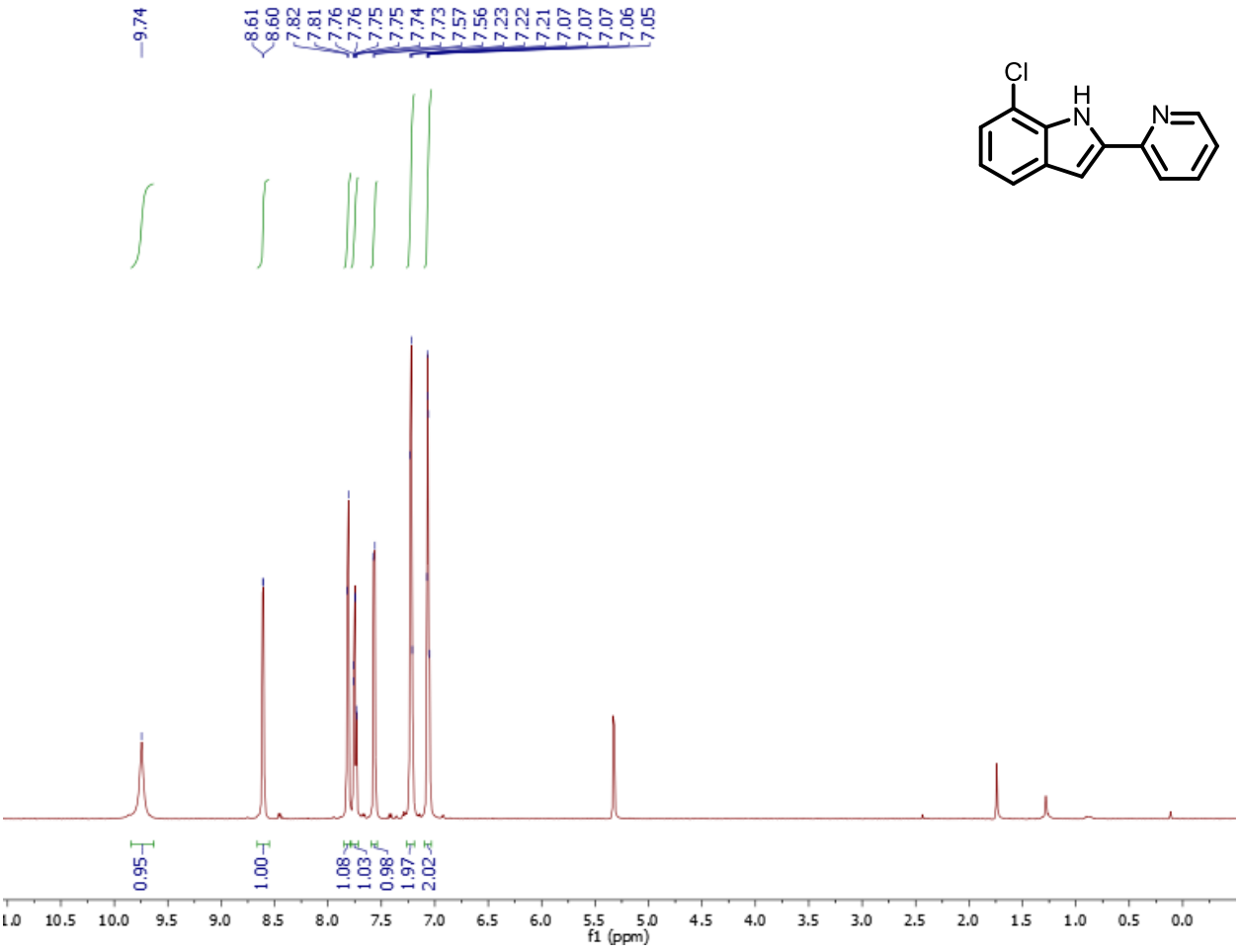


**Figure S86**. $^{13}C\{^{1}H\}$NMR of **1j** in $CD_2Cl_2$.

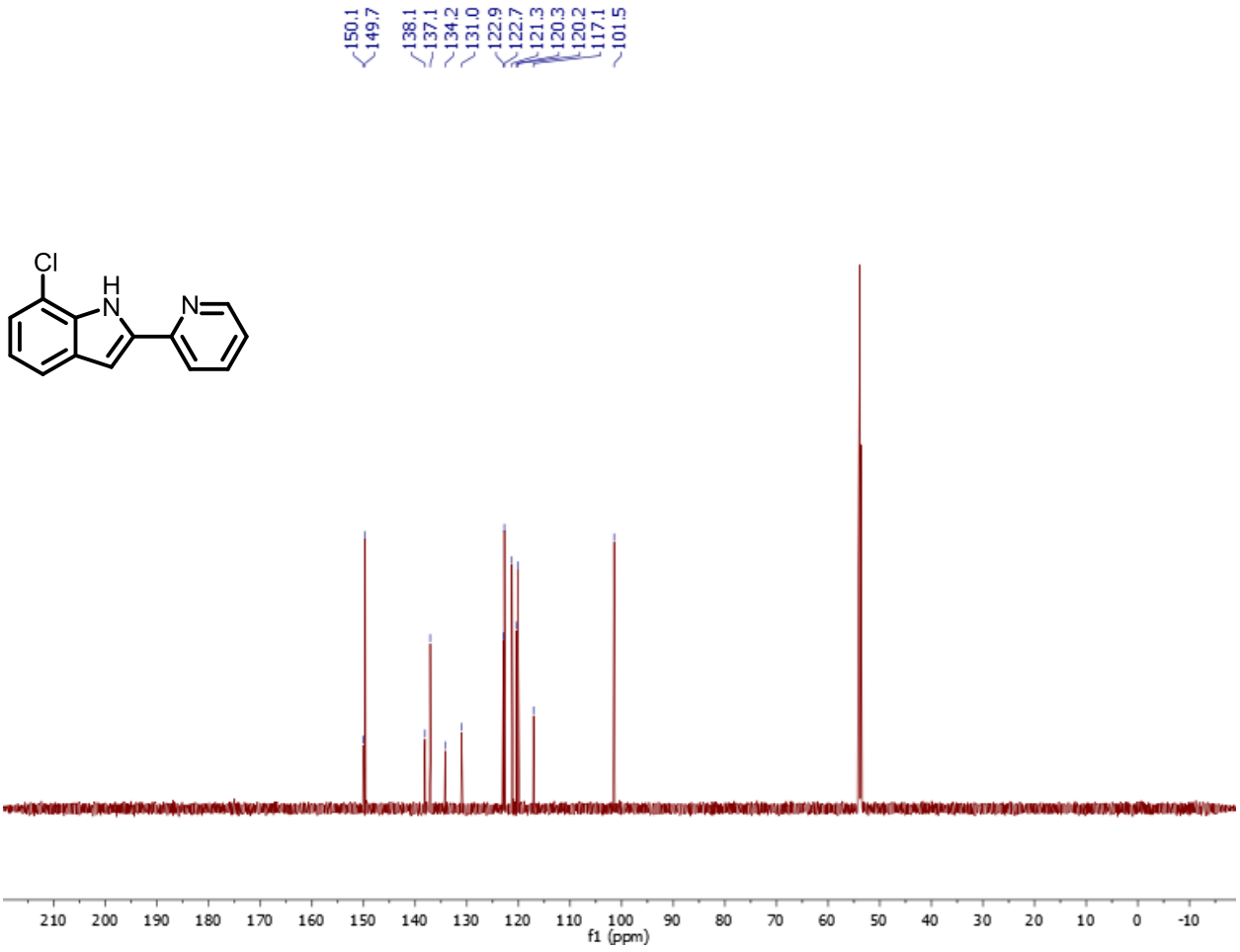


**Figure S87**. $^{1}$H NMR of **2j** in $CD_2Cl_2$. Insert: expansion from 7.90 to 6.70 ppm.

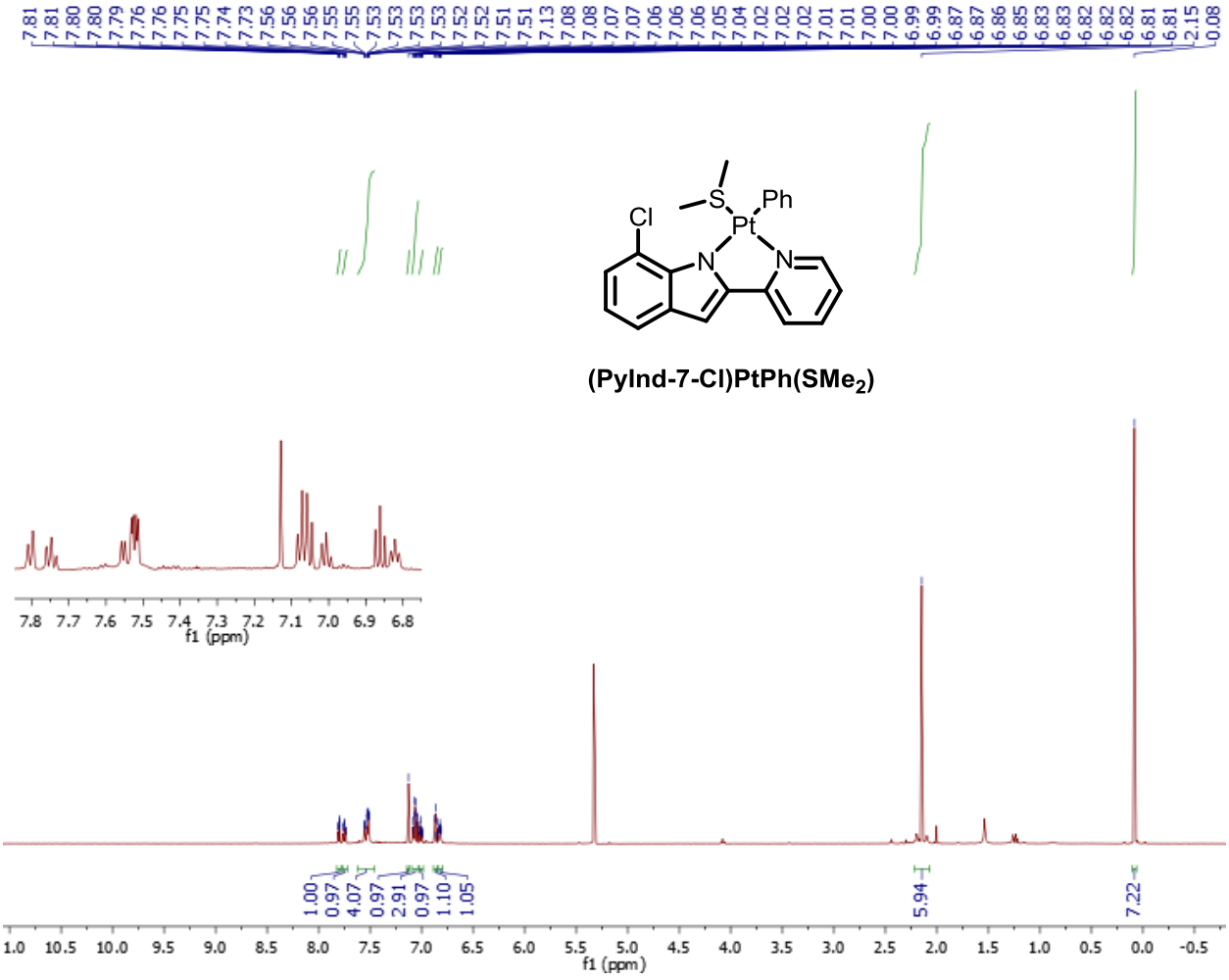


**Figure S88**. $^{13}C\{^{1}H\}$ NMR of **2j** in $CD_2Cl_2$. Insert: expansion from 170.0 to 130.0 ppm.

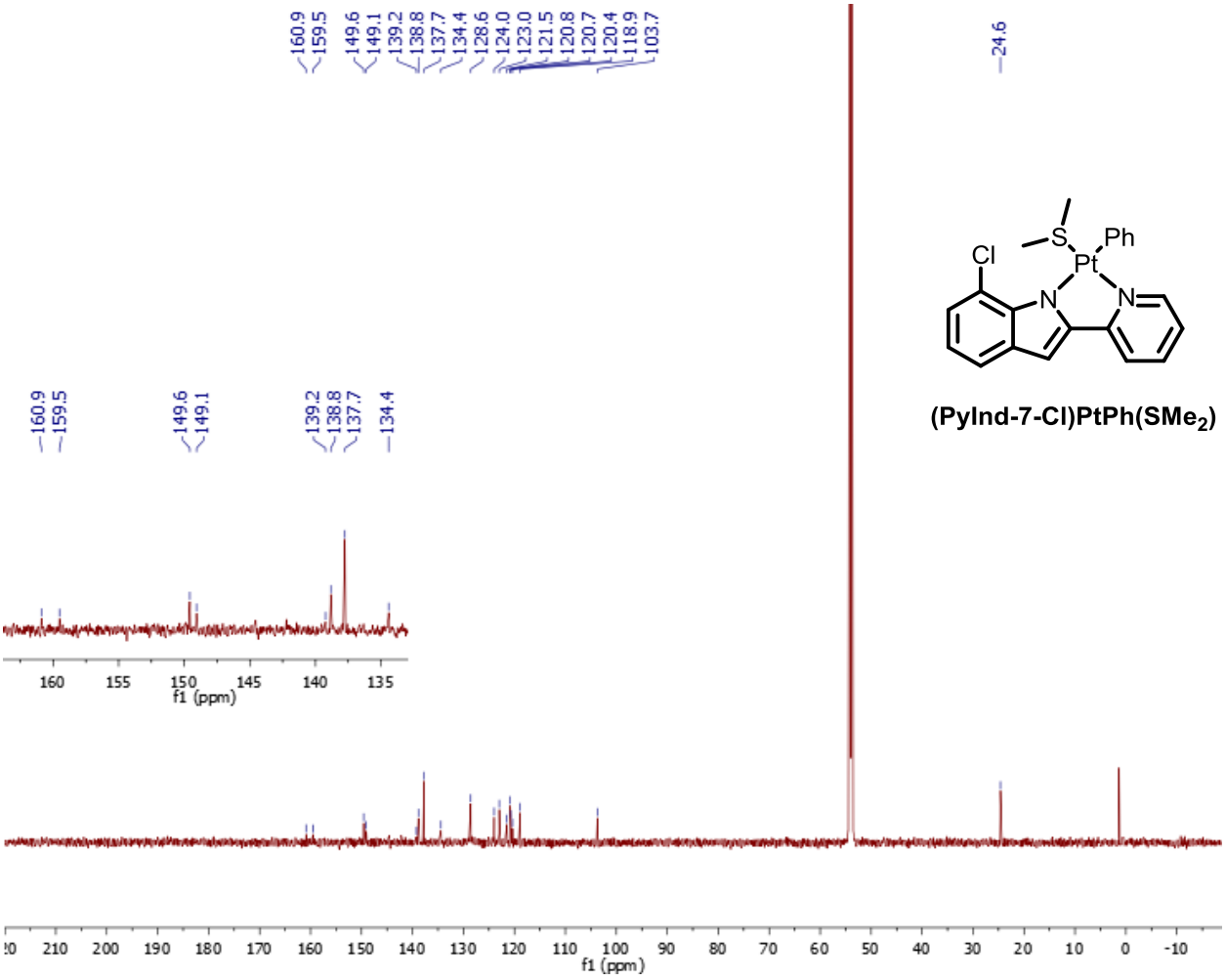


**Figure S89**. $^{1}$H NMR of **2k** in $CD_2Cl_2$. Top insert: expansion of arene $^{1}$H resonances from 8.40 to 6.50 ppm. Bottom insert: expansion of $^{1}$H resonances from 2.80 to 1.0 ppm corresponding to $SEt_2$ protons.

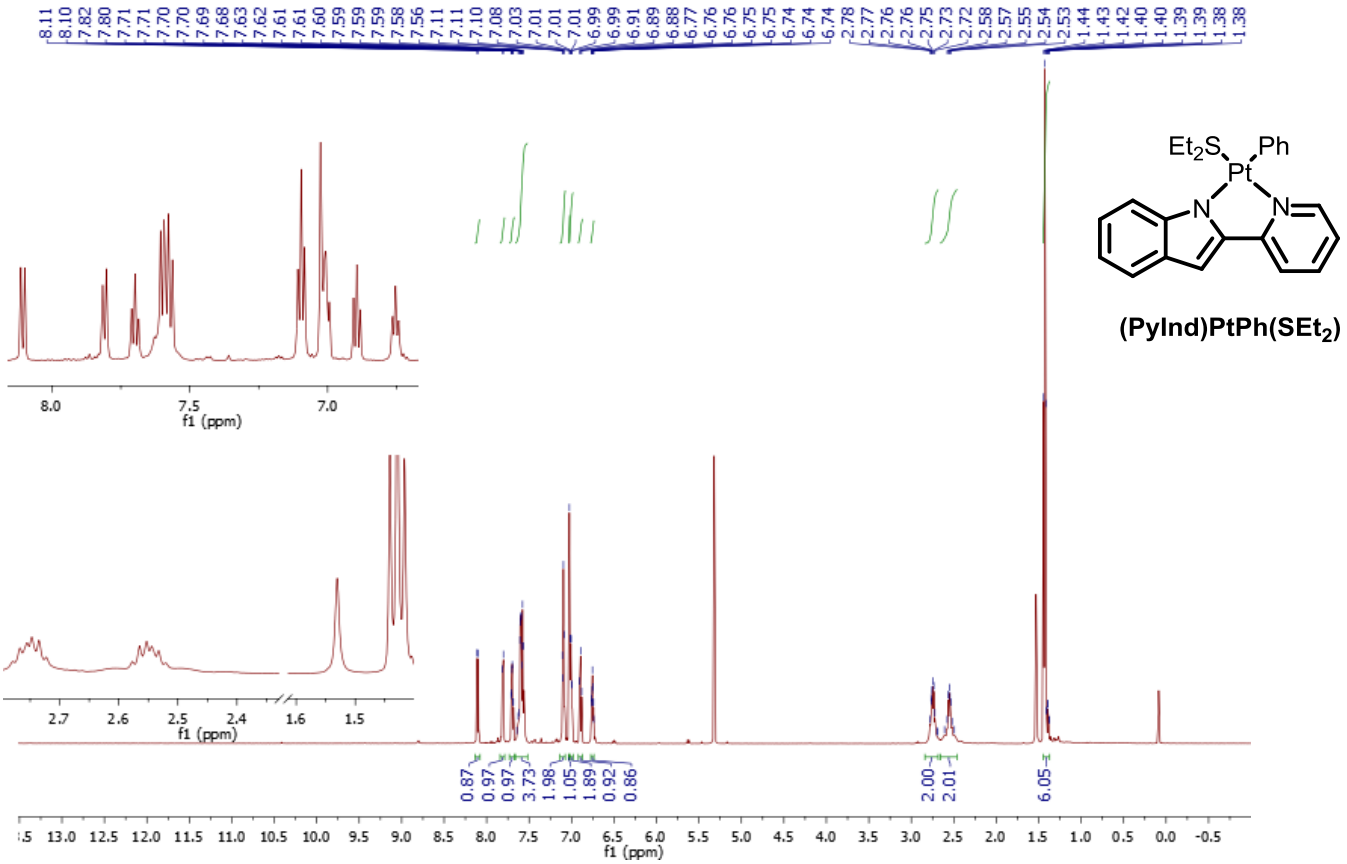


**Figure S90**. $^{13}C\{^{1}H\}$ NMR of **2k** in $CD_2Cl_2$.

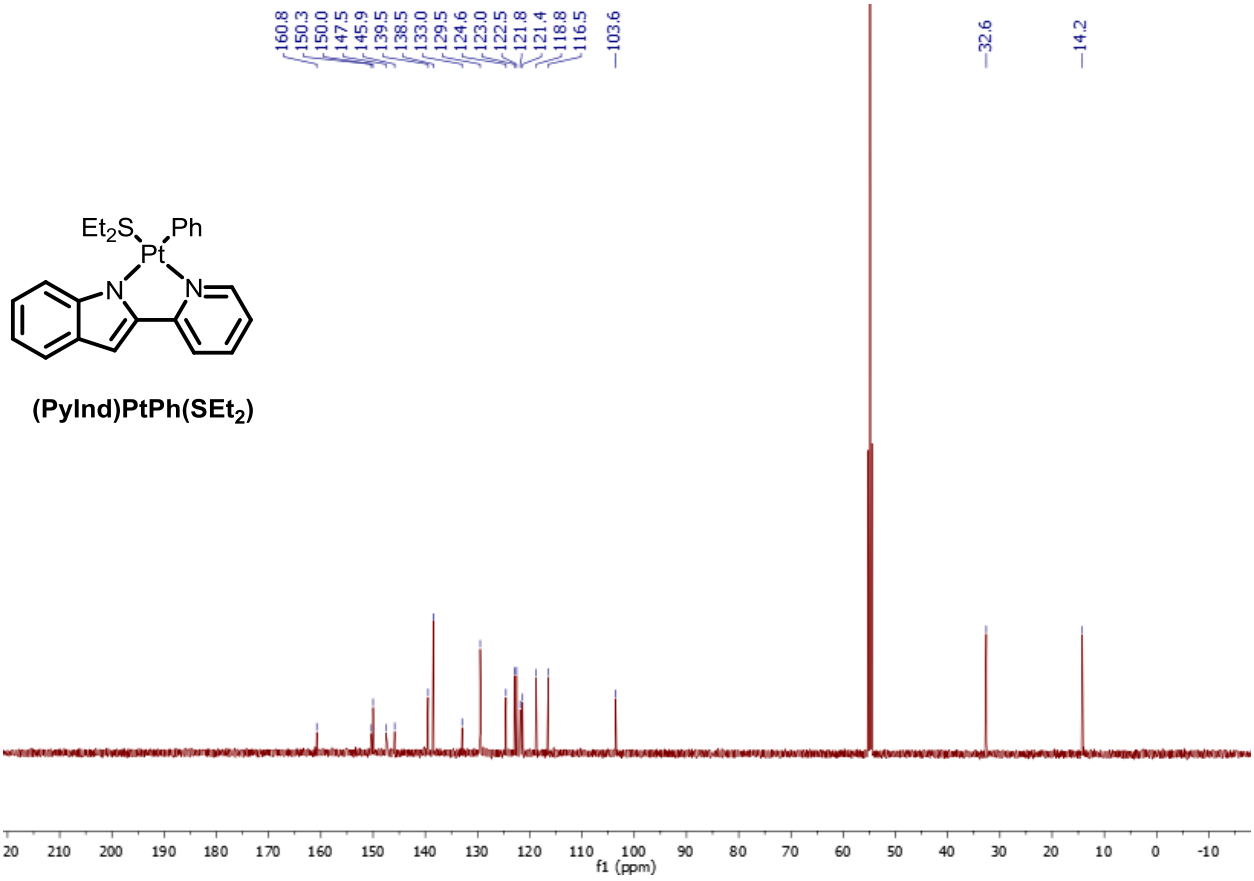


**Figure S91**. $^{1}$H NMR of **3** in $CD_2Cl_2$.

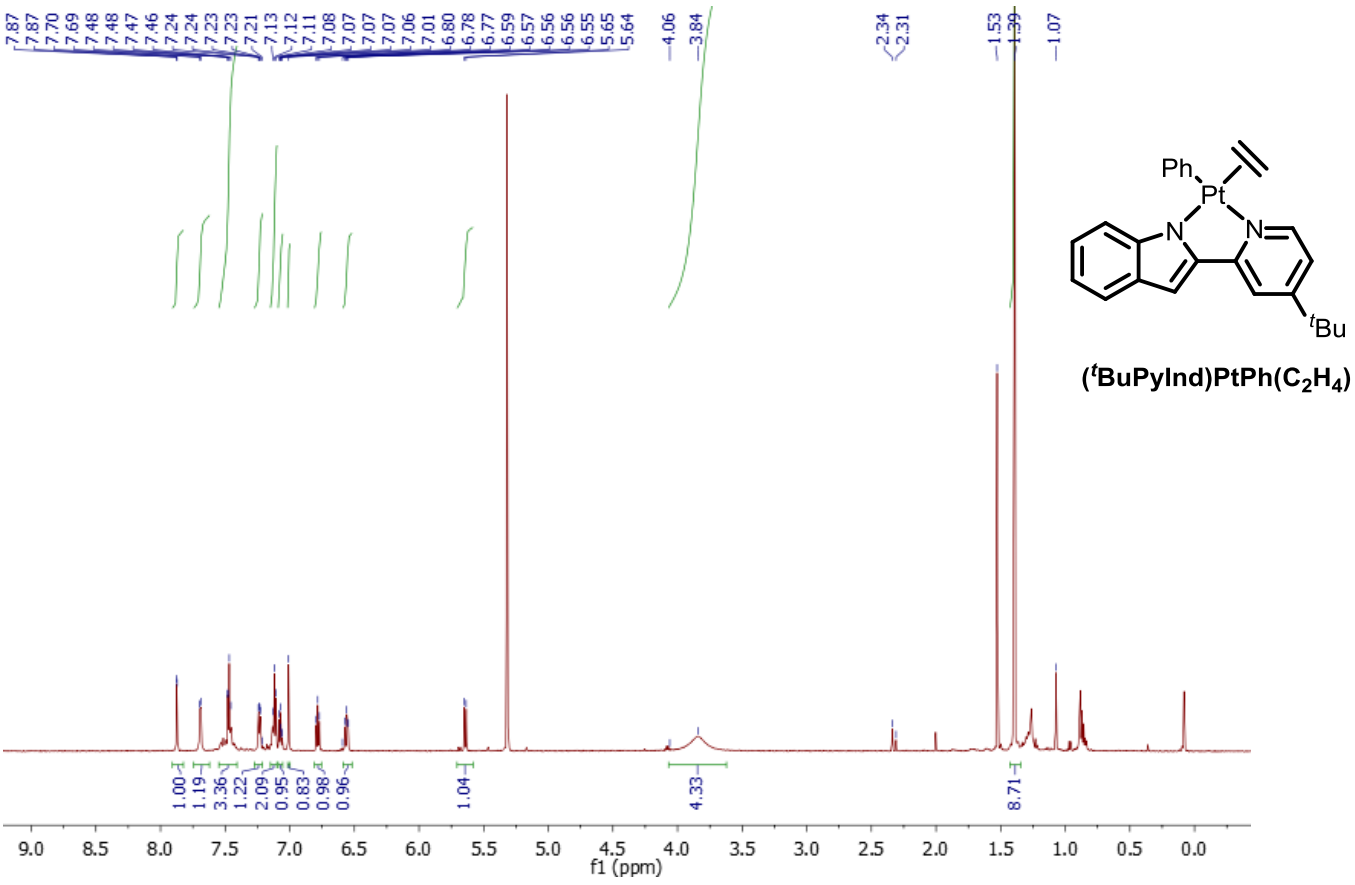


**Figure S92**. $^{13}C\{^{1}H\}$ NMR of **3** in $CD_2Cl_2$. Insert: expansion from 165.0 to 133.0 ppm.

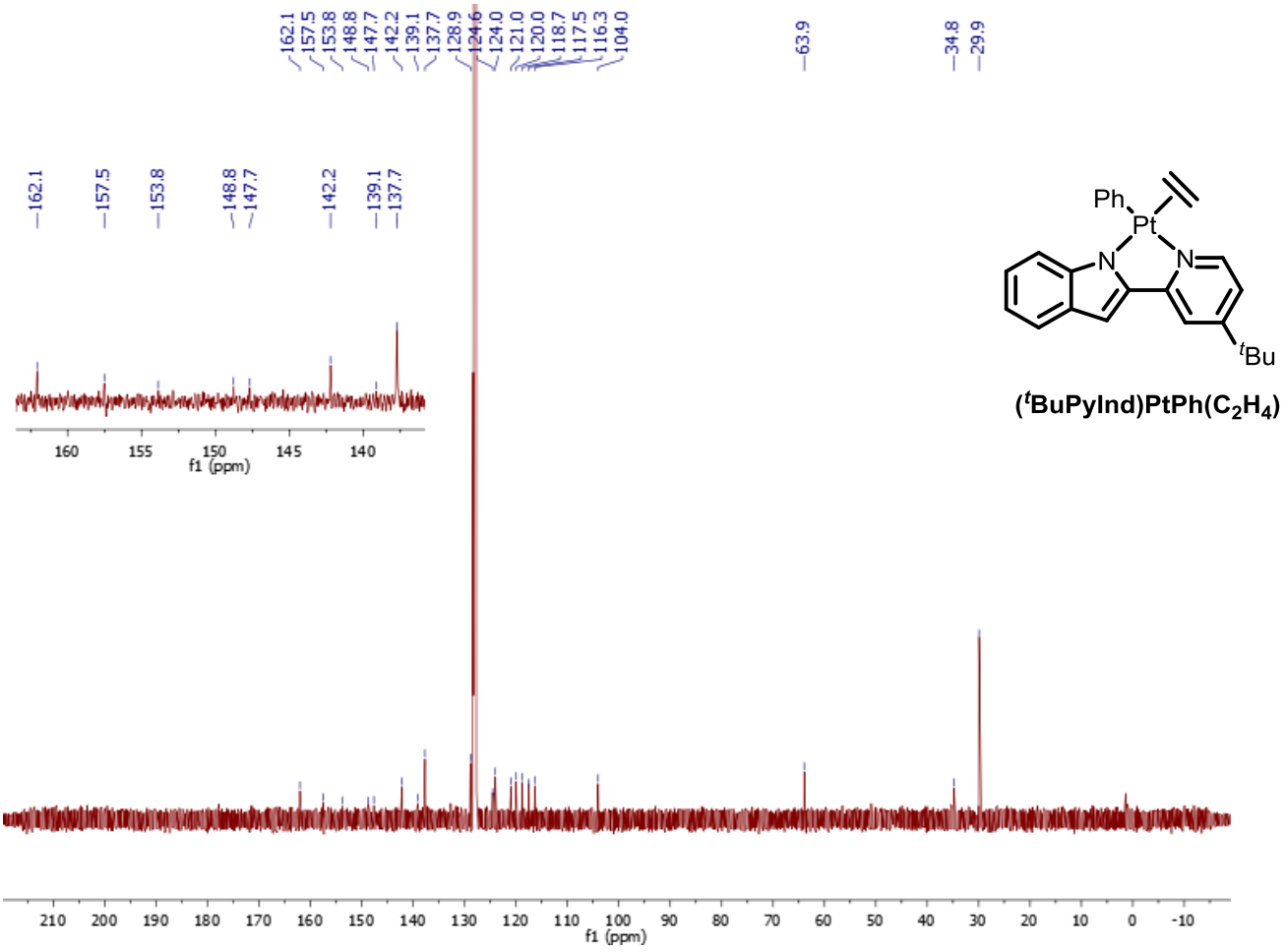


**Figure S93**. $^{1}$H NMR of **4** in $C_6D_6$. Insert: expansion of aliphatic $^{1}$H resonances from 3.30 to 1.80 ppm.

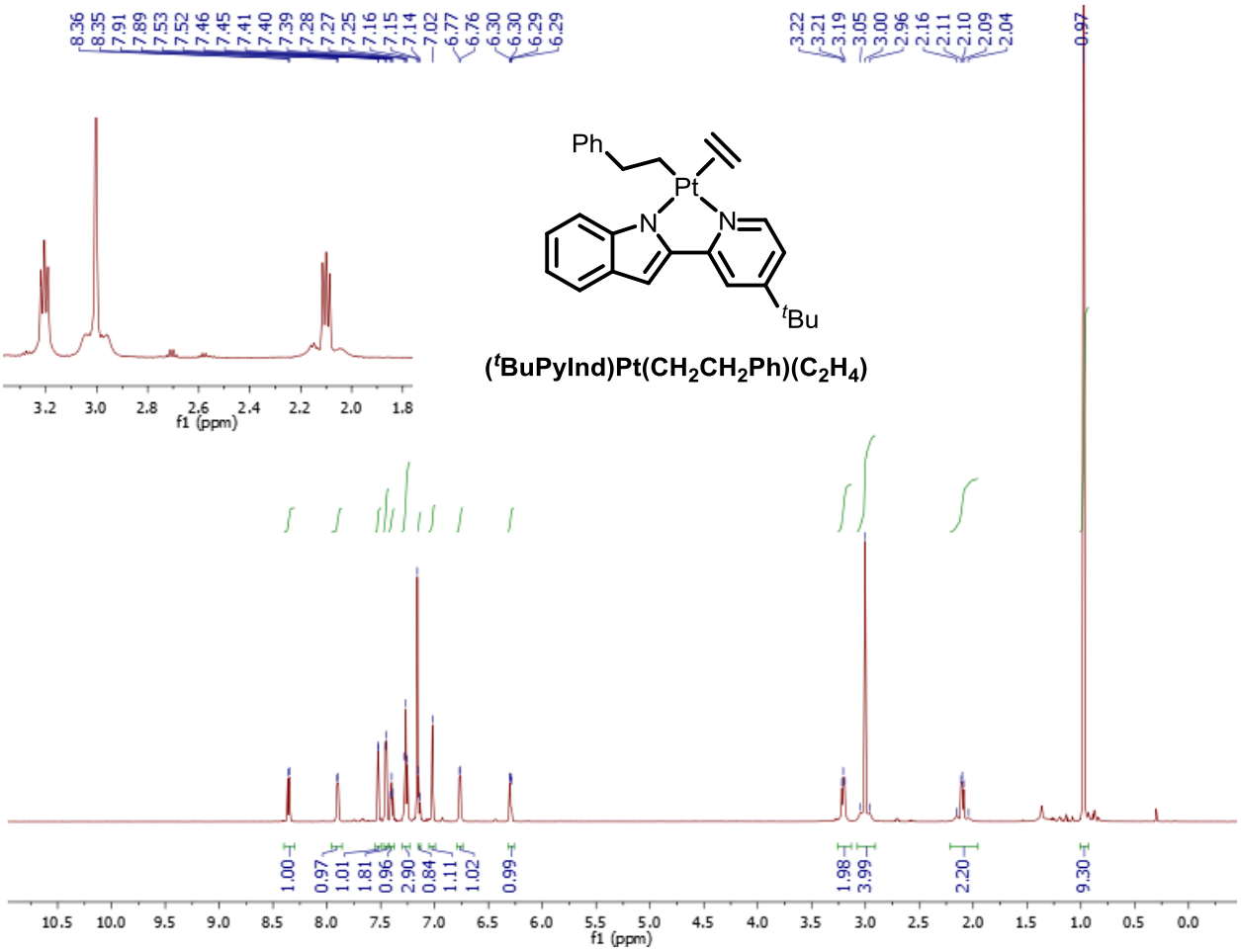
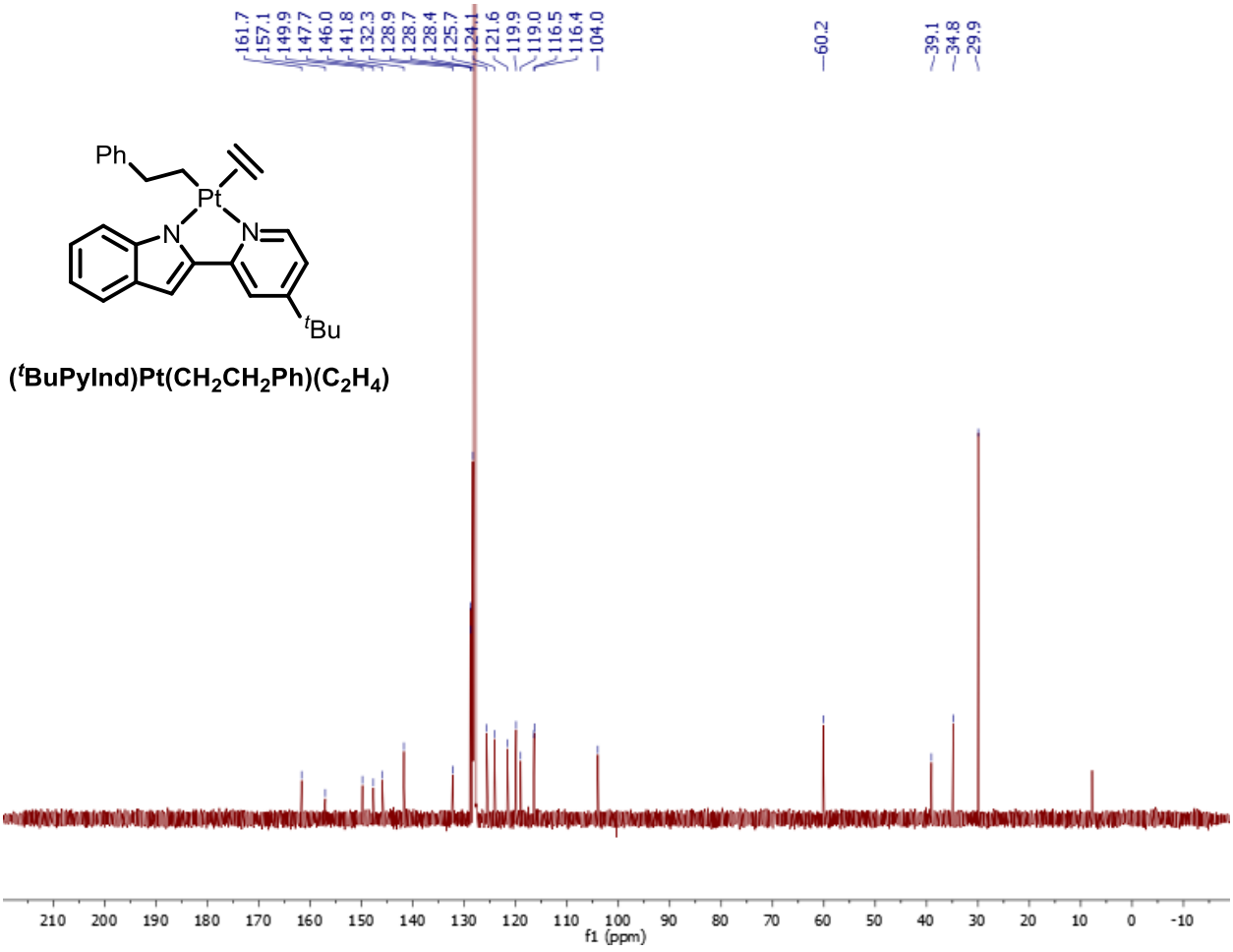


**Figure S94**. $^{13}C\{^{1}H\}$ NMR of **4** in $C_6D_6$.



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